VOL. XXVII. JANUARY, 1902. NO. 1.

AMERICAN

CHEMICAL JOURNAL

METHYL DERIVATIVES OF INDIGO.

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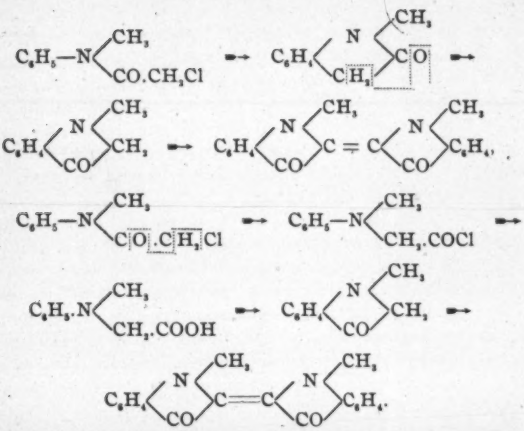
I. GENERAL CONSIDERATIONS.

In our last article[1] it was shown that Flimm's[2] synthesis of indigo, which consists of the fusion of bromacetanilide with dry caustic potash, may satisfactorily be explained by assuming the formation of diphenyldiketopiperazine as an intermediate product, since, in fact, indigo can be formed from the latter as well as from bromacetanilide.

If our view be correct, those substituted brom- or chloracetanilides which are so constituted as not to be able to form the piperazine ring would not yield the substituted indigos. According to Flimm,[3] indigo is formed from bromacetanilide by molecular rearrangement, through the intermediate stage of pseudoindoxyl. Heumann[4] believed that phenylglycocoll bromide and then pseudoindoxyl are first formed. If this be true, a substituted brom- or chloracetanilide, such as methylchloracetanilide, ought to yield dimethylindigo in which the methyl groups have replaced the hydrogen atoms of the imido groups, as will be assumed:

[1] This JOURNAL, 24, 167.
[2] Ber. d. chem. Ges., 23, 57.
[3] *Loc. cit.*
[4] *Ibid.*, 23, 3045.



Now, in order to decide the points in question, the authors have specially prepared methylchloracetanilide,

$$C_6H_5—N(CH_3).CO.CH_2Cl,$$

which is considered to be chloracetanilide in which the hydrogen of the imido group has been replaced by methyl, and hence it can not form the piperazine ring. It was then subjected to fusion with caustic potash and found to decompose entirely, not giving a trace of indigo derivatives. Its deportment towards the fused potash was apparently different from that of ordinary chloracetanilide. Flimm[1] also states that phenylchloracetanilide,

$$C_6H_5.N.C_6H_5.CO.CH_2Cl,$$

prepared from diphenylamine and chloracetyl chloride did not give phenyl derivatives of indigo at all under similar treatment. The authors repeated his experiments and obtained the same results, which must be due, as they believe, to the impossibility of the formation of the piperazine ring.

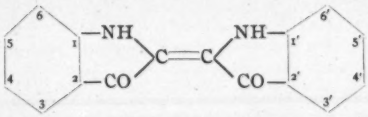
There is another fact which may support the author's view.

[1] *Loc cit.*

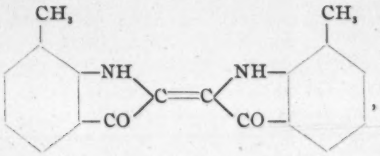
Hausdörfer[1] claims that he obtained phenylglycocoll by treating diphenyldiketopiperazine with alcoholic potash; we followed his method with diorthotolyldiketopiperazine and succeeded in getting a very small quantity of orthotolylglycocoll. Now we maintain that phenylglycocoll may be formed from diphenyldiketopiperazine by the action of fused caustic potash just as it is when alcoholic potash is used, and that indigo is formed by its further action.

On extending this principle to the formation of the derivatives of indigo, we succeeded in getting the different methyl derivatives. The experiments were conducted with chloracetyl derivatives of ortho, meta- and paratoluidines as well as with diortho- and diparatolyldiketopiperazines, dimethylindigo being obtained in each case. And also with chloracet-*unsym.*-metaxylide and chloracetpseudocumidide, and with their corresponding diaryldiketopiperazines, tetra- and hexamethylindigos were obtained.

For designating the positions of methyl groups in different methyl indigos, we propose to number the carbon atoms in the two benzene nuclei of indigo, as shown in the following formula:

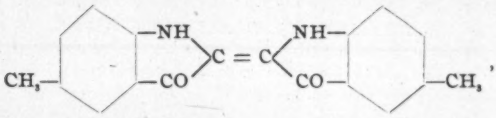


As only one dimethylindigo is possible from either diorthotolyldiketopiperazine (or chloracetorthotoluide) or diparatolyldiketopiperazine (or chloracetparatoluide), we believe that the dimethylindigo from the former has the structure



[1] Ber. d. chem. Ges., **22**, 1802.

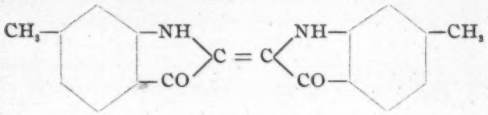
and we call it 6.6′-dimethyl indigo, while from the latter we get



which is 4.4′ dimethylindigo.

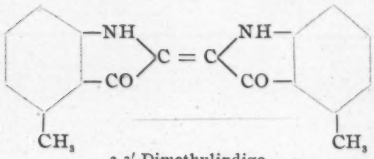
Three isomeric forms are possible from dimetatolyldiketo-piperazine (or chloracetmetatoluide) :

I.



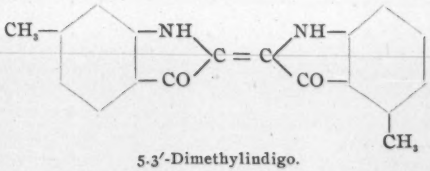
5.5′-Dimethylindigo.

II.



3.3′-Dimethylindigo.

III.

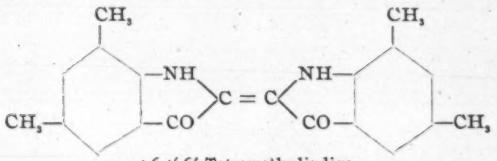


5.3′-Dimethylindigo.

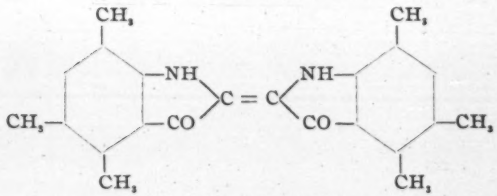
We must decide which of these three formulas corresponds to the dimethylindigo obtained by us from chloracetmeta-toluide. Based upon the rules of orientation universally accepted, the CO group enters the para position, with reference

to the CH_3 group, more readily than the ortho position, and hence the dimethylindigo of the formula (I.), or 5.5′-dimethylindigo, may be the principal product of the reaction.

Tetra- and hexamethylindigos, formed respectively from di-*unsym.*-metaxylyldiketopiperazine or chloracet-*unsym.*-metaxylide, and dipseudocumyldiketopiperazine, or chloracetpseudocumidide, must evidently possess the following structures:



4.6,4′.6′-Tetramethylindigo.



3.4.6,3′.4′.6′-Hexamethylindigo.

On referring to the literature, we find the different methyl derivatives of indigo which are already known. Dimethylindigo obtained by Flimm[1] from bromacetparatoluide, and by Eckenroth[2] from chloracetparatoluide, the so-called *p*-dimethylindigo, lately prepared by Kunckell[3] from *p*-methyl-*o*-acetylamidochloracetophenone, and 4.4′-dimethylindigo made by the authors from diparatolyldiketopiperazine are all identical. So-called metamethylindigo[4] was also prepared at Farbewerke vorm. Meister, Lucius and Brüning from orthonitrometamethylbenzaldehyde, but its constitution is quite

[1] Ber. d. chem. Ges., **23**, 59.
[2] *Ibid.*, **24**, 693.
[3] *Ibid.*, **33**, 2648.
[4] *Ibid.*, **16**, 817 (Ber. ü. Pat.).

obscure, because, though it should be identical with either 4.4′- or 6.6′-dimethylindigo, interpreting its formation from the theoretical standpoint, it shows an entirely different spectrum from either of the other two, and consequently must possess a different structure. Flimm once tried to get an isomeric dimethylindigo from chloracetorthotoluide by the potash fusion, but, having been unsuccessful, he ascribes the failure to the presence of one of the ortho positions previously occupied by a methyl group. But the substance, like indigo, obtained from orthotolylglycocoll by the potash fusion at the Badische Anilin- und Soda-Fabrik[1] may be identical with our 6.6′-dimethylindigo prepared from diorthotolyldiketopiperazine or chloracetorthotoluide. And an indigo derivative obtained also at the Badische Anilin- und Soda-Fabrik[2] from metaxylylglycocoll and 4.6,4′.6′-tetramethylindigo obtained by us from di-*unsym.*-metaxylyldiketopiperazine or chloracet-*unsym.*-metaxylide, may possibly be identical.

Besides the formation of indigo or its methyl derivatives, as the principal reactions, from diphenyldiketopiperazine or ditolyldiketopiperazines, we have observed the production of phenylisonitril, potassium carbonate, and primary and secondary amines, just as in the case of Heumann's synthesis. We thus have further proof that diaryldiketopiperazine may break down into arylglycocoll, which, in turn, would undergo changes as in Heumann's process.

II. METHYLCHLORACETANILIDE,

$$C_6H_5—N\begin{matrix}CH_3\\ \diagup\\ \diagdown\\ CO.CH_2Cl\end{matrix}.$$

This substance has not been known hitherto. At first methylaniline was prepared according to Hepp's[3] method. On mixing it with chloracetyl chloride, each in well-cooled ethereal solution, methylchloracetanilide was obtained in the form of a crystalline powder. It crystallizes from hot water, on cooling, in the form of fine needles, but sometimes in large

[1] Ber. d. chem. Ges., 25, Ref. 488 (Ber. ü Pat.).
[2] *Loc. cit.*
[3] Ber. d. chem. Ges., 10, 327.

prisms from its dilute solution. It sublimes when heated and attacks the skin to some extent. The melting-point of the crystals is 61°. The crystals dried between the folds of filter-paper, or kept in a desiccator for a few days, gave, on analysis, the following results:

I. 0.4374 gram substance gave 0.0813 gram Cl.
II. 0.4998 gram substance gave 0.0919 gram Cl.

	Calculated for $(ClCH_2.CO.N.CH_3.C_6H_5)_2.H_2O$.	Found. I.	II.
Cl	18.44	18.59	18.39

After the crystals had been kept in a desiccator for more than a week they were again analyzed.

0.1721 gram substance gave 0.0332 gram Cl.

	Calculated for $ClCH_2.CO.N.CH_3.C_6H_5$.	Found.
Cl	19.35	19.29

Methylchloracetanilide, when fused with caustic potash, behaves quite differently from chloracetanilide or chloracettoluide. It never yields substances related to indigo but decomposes entirely.

III. DIMETHYLINDIGOS.

The chloracetorthotoluide used in the experiments was prepared according to the directions given by Abenius and Widman,[1] whose process consists in mixing 1 molecule chloracetyl chloride with 2 molecules orthotoluidine, each in well cooled ethereal solution. P. Meyer[2] recommends benzene as a solvent instead of ether. We have, however, found it more advantageous, as we believe, to use the ethereal solutions of the two substances cooled with ice, so as to give the theoretical yield of the product.

Chloracetmetatoluide has not been described in the literature hitherto. For its preparation exactly the same process as above given was used. The substance was purified by repeated recrystallization from hot water and dried over calcium chloride, and its chlorine was determined.

[1] J. prakt. Chem. [2], 38, 299.
[2] Ber. d. chem. Ges., 8, 1154.

I. 0.2510 gram substance gave 0.0481 gram Cl.
II. 0.2162 gram substance gave 0.0411 gram Cl.

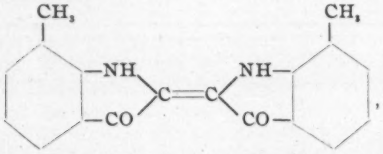
	Calculated for $CH_3.C_6H_4.NH.CO.CH_2Cl$.	Found. I.	II.
Cl	19.35	19.17	19.05

It melts at 141°. It is somewhat volatile, even at ordinary temperatures, and sublimes when heated. Its property of attacking the skin, its solubility, and other properties are similar to those of the orthotoluide.

Chloracetparatoluide was prepared by Tommasi,[1] by Eckenroth and Donner,[2] and by Meyer.[3] It was also prepared in the same way as the isomeric toluides.

From chloracetorthotoluide and chloracetparatoluide diortho- and diparatolyldiketopiperazines were prepared, respectively, by the process suggested by Abenius.[4] We were, however, not able to get dimetatolyldiketopiperazine, since only a few grams of chloracetmetatoluide were at hand. These diaryldiketopiperazines readily yield dimethylindigos.

1. 6.6′-Dimethylindigo,



was easily formed from diorthotolyldiketopiperazine as well as from chloracetorthotoluide by fusing with caustic potash.

Flimm states that he failed to get dimethylindigo from chloracetorthotoluide by fusing with caustic potash, but, on the contrary, we found that it could be formed from chloracetorthotoluide, and also from its corresponding ditolyldiketopiperazine, with a tolerably good yield. We mixed chloracetorthotoluide with an equal volume of dry powdered caustic potash, and heated the mixture in a test-tube or flask.

[1] Bull. soc. chim., **19**, 400.
[2] Ber. d. chem. Ges., **23**, 3757.
[3] *Ibid.*, **8**, 1154.
[4] *Ibid.*, **21**, 1665.

The mixture instantly assumed a reddish-yellow color, when the potash began to fuse, then turned pale-yellow and reddish-brown, and finally changed to greenish-yellow on cooling. The mass was now treated with water, and from the solution dimethylindigo precipitated immediately on exposure to the air. Its production was shown to be dependent wholly upon the nature of the caustic potash used. When containing potassium carbonate, it was found to give the best result, and after several trials the following proportions of the materials were found to be most favorable:

Chloracetorthotoluide	100 parts
Dry powdered caustic potash	175 "
Potassium carbonate	25 "

Without mixing any potassium carbonate intentionally the yield of the dimethylindigo was very poor or often none. Its action is, however, not quite certain, but its presence may probably keep the mixture from being entirely fused when heated, thus avoiding the free access of air, and also preventing too violent an action of the potash which would, in that case, be destructive. The use of a glass vessel should be avoided for the fusion, since it is rapidly corroded by the melted potash. Thus a nickel crucible was substituted with the following precautions: A square box of asbestos-board, having a hole at its bottom just large enough to allow the crucible to rest over it, was constructed, and a cover of the same material was made to fit. A gas flame was applied from below, so as to heat directly the bottom of the crucible. We at first thought it best to pass nitrogen gas into the box in order to prevent the oxidation of the product, but soon found it unnecessary to do so in consequence of the evolution of heavy vapors which fill the box and exclude air. The reactions proceed smoothly.

For the purification of the dimethylindigo so obtained several methods were tried, and at last we found it most advantageous to filter the precipitate of dimethylindigo and to wash successively with hot water and alcohol, the latter completely dissolving out the resinous matter. For analysis we had to sublime it under 35 to 40 mm. pressure, according to

Sommaruga.[1] The sublimate was again washed with alcohol and ether to get rid of heavy hydrocarbons which may possibly have been formed by the decomposition of the dimethylindigo. Precipitated dimethylindigo can also be purified by washing with alcohol, then dissolving in hot chloroform, and removing the residue from the solution. This process is most convenient for purifying from silica which is derived from the glass vessels used.

Sublimed dimethylindigo was analyzed by Dumas' method.

I. 0.3158 gram substance gave 25.7 cc. nitrogen at 14° C. and 756.7 mm. pressure.

II. 0.2158 gram substance gave 17.9 cc. nitrogen at 20° C. and 756.4 mm. pressure.

	Calculated for $CH_3.C_6H_5\langle^{CO}_{NH}\rangle C:C\langle^{CO}_{NH}\rangle C_6H_5.CH_3$.	Found. I.	II.
N	9.66	9.53	9.47

6.6′-Dimethylindigo is a powder when precipitated but, when sublimed, it crystallizes in prisms very closely resembling ordinary indigo in appearance. It gives a bright violet vapor with partial decomposition when heated. Its characteristic property is its solubility in various solvents. One gram of the substance is soluble in about 2000 cc. alcohol and in 500 cc. chloroform. It is more or less soluble in ether, aniline, benzene, nitrobenzene, oil of turpentine, fused chloralhydrate, paraffin, linseed oil, acetic acid, and fuming sulphuric acid, and is, in general, more soluble than ordinary indigo. The colors of the solutions in these solvents vary from reddish-violet to green or blue. We observed the absorption band of the chloroform solution according to the statements of Krüss and Oeconomides,[2] seeking for the position of maximum darkness. When the solution is highly concentrated or its layer is thick, the absorption takes place from orange to green, while with ordinary indigo the range is much less. The results of our observations are given at the end of the paper.

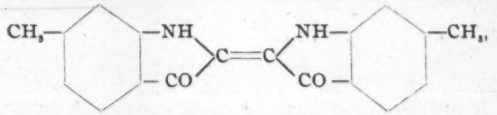
[1] Ber. d. chem. Ges., 11, 1355.

[2] *Ibid.*, 16, 2051.

In order to examine the products of the secondary reactions, we collected the fumes evolved during the fusion by passing them into a vessel containing water. Oily drops suspended in water were found to be orthotoluidine and methylorthotoluidine.

It is unnecessary to describe the fusion of diorthotolyldiketopiperazine here, because its behavior toward caustic potash is precisely the same as that of chloracetorthotoluide. The dimethylindigo formed agrees in all respects with that from chloracetorthotoluide.

2. 5.5′-Dimethylindigo,



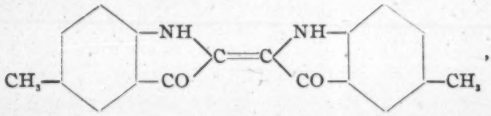
was formed from chloracetmetatoluide by the same method as its isomers, but the conditions of fusion were apparently different from the former cases. It seems strange that in this case the addition of potassium carbonate to the caustic potash was of no benefit; this may, however, be due to the high melting-point of dimetatolyldiketopiperazine which is formed as an intermediate product in the reaction. Although we could not prepare it, as the quantity of chloracetmetatoluide at hand was very small, yet we infer that its melting-point may be higher than that of the ortho compound, as will be seen from the following data:

	Melting-point.
Chloracetorthotoluide	111° to 112°
Chloracetmetatoluide	141°
Chloracetparatoluide	161°.5
Diorthotolyldiketopiperazine	159° to 160°
Dimetatolyldiketopiperazine	....
Diparatolyldiketopiperazine	252° to 253°

5.5′-Dimethylindigo resembles its isomers in its properties. It is soluble in alcohol, ether, chloroform, etc. Its solubility in chloroform is about 1 : 1000. It differs somewhat from its

isomers in the absorption band, as will be seen from the annexed table.

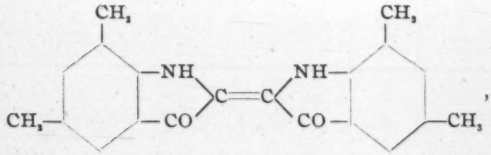
3. 4.4′-Dimethylindigo,



was formed from diparatolyldiketopiperazine and also from chloracetparatoluide under the same conditions as the meta compound. Ir was found to be identical with the dimethylindigo already known, as explained in the preceding part of the paper. Its solubility in chloroform is almost the same as that of 5.5′-dimethylindigo.

IV. TETRAMETHYLINDIGO.

4.6,4′.6′-Tetramethylindigo,



was formed from chloracet-*unsym.*-metaxylide and from di-*unsym.*-metaxyldiketopiperazine by fusing with caustic potash. Its properties are similar, in many respects, to those of the other methyl derivatives of indigo. Its solubilities and the position of the absorption band are given in the table below.

Chloracet-*unsym.*-metaxylide was prepared by mixing 100 grams of *unsym.*-metaxylidine and 50 grams of chloracetyl chloride, each dissolved in benzene. The yield was almost theoretical. It crystallizes in silky needles from benzene, and does not attack the skin. Its melting-point is 143°. The substance was analyzed with the following results:

I. 0.1141 gram substance gave 0.0204 gram Cl.
II. 0.1532 gram substance gave 0.0274 gram Cl.

	Calculated for $ClCH_2.CO.NH.C_6H_3(CH_3)_2$.	Found. I.	II.
Cl	17.97	17.88	17.92

It produced di-*unsym.*-metaxlyldiketopiperazine by treating with alcoholic potash, as in the preparation of other diaryldiketopiperazines. It crystallizes in colorless needles and melts at 170°.

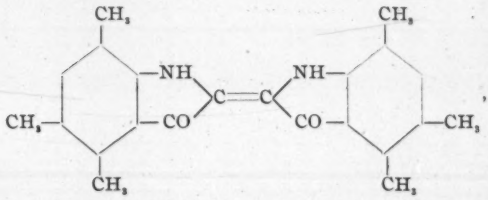
V. HEXAMETHYLINDIGO.

Chloracetpseudocumidide was prepared from pseudocumidine and chloracetyl chloride. It crystallizes in needles and melts at 158°.5. Its analytical results are as follows:

	Calculated for $Cl.CH_2.CO.NH.C_6H_2(CH_3)_3$.	Found.
Cl	16.79	17.00

Dipseudocumyldiketopiperazine formed from the above substance crystallizes in colorless needles and melts at 221°.5.

A corresponding methyl derivative of indigo, or 3.4.6, 3′.4′.6′.-hexamethylindigo,



was obtained from chloracetpseudocumidide as well as from dipseudocumyldiketopiperazine, but only in small quantity.

Positions of the Maximum Darkness in the Absorption Bands of the Methylindigos. (*Chloroform Solution.*)

Name.	λ_1.	λ_2.	$\frac{\lambda_1+\lambda_2}{2}$.
Ordinary indigo	622.7	587.6	605.1[1]
6.6′-Dimethylindigo	643.6	615.7	629.7
5.5′-Dimethylindigo	619.2	598.1	608.6
4.4′-Dimethylindigo	643.7	622.7	633.2
4.6,4′.6′-Tetramethylindigo	662.7	631.7	647.2

[1] Krüss and Oeconomides give $\frac{\lambda_1+\lambda_2}{2}$ = 604.8 for ordinary indigo.

Solubilities of the Methylindigos in Various Solvents.

Solvents.	Ordinary indigo.	6.6'-Dimethylindigo.	5.5'-Dimethylindigo.	4.4'-Dimethylindigo.	4.6,4'.6'-Tetramethyl-indigo.
Alcohol	Insoluble	Soluble in cold; easily in hot with deep-blue color	Soluble with blue color	Soluble with blue color	Soluble with blue color
Ether	Insoluble	Soluble in cold with violet color	Sol'ble with reddish-violet color	Soluble with blue color	Less soluble with blue color
Chloroform	Slightly soluble with violet color	Easily soluble with violet color	Readily soluble with reddish-blue color	Readily soluble with blue color	Easily soluble with deep-blue color
Aniline	Slightly soluble in hot with bluish-green color	Soluble in cold with bluish-green color	Soluble with greenish-blue color	Soluble with green color	Soluble with green color
Nitrobenzene	Insol'ble in cold; soluble in hot with violet color	Difficultly soluble in cold, readily in hot with violet color	Soluble with green color	Slightly soluble with green color	Soluble with green color
Turpentine oil	Ins'l'ble in cold; slightly soluble in hot, but soon decolorizes	Slightly soluble in cold, more so in hot, but soon decolorizes	Soluble with blue color (slightly reddish) but soon decolorizes	S'l'ble, but soon decolorizes	Soluble with light-blue color but soon decolorizes

Solubility of the Methylindigos in Various Solvents (Continued).

Solvents.	Ordinary indigo.	6.6-Dimethylindigo.	5.5'-Dimethylindigo.	4.4'-Dimethylindigo.	4.6,4'.6'-Tetramethylindigo.
Chloral hydrate (melt'd)	Soluble with deep-blue color	Readily soluble with greenish-blue color	Soluble with dark-blue color	Readily soluble with bright-blue color	Moderately soluble with greenish-blue color
Paraffin (melt'd)	Slightly soluble with amethyst color	Sol'ble with violet color	Soluble with bright-violet color	Soluble with blue color	Sol'ble with violet color
Linseed oil	Sol'ble with violet color	S'l'ble with reddish-violet color	Soluble with reddish-blue color	Soluble with green color	Soluble with greenish-blue color
Acetic acid	Ins'l'ble in cold; slightly soluble in hot with blue color	Difficultly soluble in cold, readily in hot with blue color	Soluble with bright-blue col'r	Soluble with blue color	Soluble with blue color
Benzene	Slightly soluble in hot with amethyst color	Soluble in cold, readily in hot with violet color	Soluble with reddish-blue color	Soluble with blue color	Soluble with bluish-violet color

THE MOLECULAR WEIGHTS OF CERTAIN SALTS IN ACETONE.

By Harry C. Jones.

Dutoit and Friderich[1] stated, in 1898, that "we have found by the boiling-point method that the following salts, NH_4CNS, $HgCl_2$, NaI, LiCl, CdI_2, dissolved in acetone have the normal molecular weights." They do not give any data, but state that their results will be published later. An examination of the literature up to the present fails to show that any such results have been published thus far.

A year later this work was cited by Kahlenberg and Lincoln,[2] who pointed out that such solutions conduct the current to a considerable degree.

Facts such as these are of special interest to-day in the light of the modern theory of solutions. If a salt dissolved in any solvent should give a normal molecular weight over a wide range of dilution, and at the same time show a large molecular conductivity which would increase with the dilution, it would, indeed, be awkward for the theory of electrolytic dissociation in its present form. However, before amending or supplementing a theory, which has correlated hundreds of apparently isolated facts, and which has probably done more towards placing chemistry upon an exact basis than any other theory which has ever been proposed, it is necessary to examine very carefully the experimental evidence bearing upon it.

Since Dutoit and Friderich have given no account of the experiments, and have not even published the data upon which their conclusion is based, I determined to study the molecular weights of some of the above substances in acetone, by means of my[3] modification of the boiling-point method of Beckmann. I proposed to determine the molecular weight at various dilutions, to see whether a normal molecular weight

[1] Bull. soc. chim. [3]. 19, 334.
[2] J. Phys. Chem., 3, 32.
[3] This Journal, 19, 581; Ztschr. phys. Chem., 31, 119.

would be obtained at any dilution, and if so, whether it would be obtained over a considerable range of dilution.

Before we can determine the molecular weight of any substance in any solvent it is necessary to know accurately the boiling-point constant of the solvent. The constant for acetone is given by Biltz[1] as 17.1. It, however, seemed desirable that this should be redetermined.

The acetone which I used in this work was a very pure sample, which was carefully freed from water. Its boiling-point, under normal pressure, was 56°.2 to 56°.4.

Boiling-Point Constant of Acetone.

In order to determine the boiling-point constant of a solvent it is necessary to select a substance which will not be dissociated by the solvent, and which will not act chemically upon it. It is also desirable that the dissolved substance should not have a very large molecular weight, in order that the rise in boiling-point should be fairly large. Naphthalene was selected as the dissolved substance since it fulfilled these conditions, and, further, could be obtained in a high degree of purity. Four determinations of the boiling-point constant of naphthalene were made, and the results are given below:

Acetone. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Constant.
55.388	1.9591	0°.480	1737
55.494	2.0465	0°.495	1718
53.698	2.6866	0°.668	1709
52.818	2.5388	0°.652	1736
		Mean,	1725

The constant for acetone is taken as the mean of the above four values, and 1725 is used in all the following calculations:

Molecular Weight of Cadmium Iodide in Acetone.

Eight determinations of the molecular weight of cadmium iodide in acetone were made, at dilutions ranging from less than 0.1 to more than 0.4 normal. The results, in the order of increasing concentration, are given below:

[1] "Practical Method for Determining Molecular Weights," p. 179.

Acetone. Grams.	CdI_2. Grams.	Grams CdI_2 in 1000 grams solvent.	Conc. normal.	Rise in boiling-point.	Molecular weight.
55.158	1.7789	32.251	0.0881	0°.124	448.6
56.031	2.0540	36.658	0.1002	0°.140	451.7
57.5065	2.4951	43.388	0.1186	0°.160	467.8
57.5065	3.7259	64.799	0.177	0°.234	477.7
56.369	3.7790	67.040	0.183	0°.236	490.1
55.923	4.5020	80.503	0.220	0°.282	492.4
57.283	5.4000	94.269	0.2576	0°.330	492.9
57.283	8.5460	149.189	0.4076	0°.504	510.7

These results show, in the first place, that the molecular weight of cadmium iodide in acetone is not normal for any of the above dilutions. It does not even approach the value 366, which corresponds to the formula CdI_2. They show, further, that the molecular weight is not a constant, but varies with the dilution used. The range of the dilutions studied is about as great as was possible by the boiling-point method. More concentrated solutions were not employed because the laws of dilute solutions do not hold at great concentrations. It would have been of interest to study more dilute solutions to see how far the molecular weight would have decreased, and whether it would have approached the normal value and have remained constant as the dilution was still further increased; but it is obvious that the rise in boiling-point would be too small to measure.

The facts then show that the molecules of cadmium iodide are polymerized to a very considerable extent in acetone, even in the most dilute solutions which were used, the complex molecules gradually breaking down into simpler molecules as the dilution is increased. But Dutoit and Aston[1] found that cadmium iodide in acetone had an appreciable conductivity. They give the following values:

Cadmium iodide	v	4	8	16	32	64	128	256
	μ_v	10.4	11.7	11.4	11.5	11.6	11.9	12.0

The conductivity is not large, and we should not expect it to be very great, since the conductivity of cadmium iodide in water is abnormally small. These conductivity values are

[1] Compt. rend., **128**, 242.

not at all at variance with the large molecular weight found since there are many cases known where we have ionization and polymerization present in the same solution. The amount of the cadmium iodide dissociated into ions is, from the above figures, not large.

Molecular Weight of Ammonium Sulphocyanate in Acetone.

Six determinations of the molecular weight of ammonium sulphocyanate in acetone, over a considerable range of dilution, gave the following results:

Acetone. Grams.	NH_4CNS. Grams.	Grams salt in 1000 grams solvent.	Conc. normal.	Rise in boiling-point.	Molecular weight.
55.647	1.1143	20.0244	0.263	0°.392	88.1
53.529	1.1082	20.7028	0.271	0°.400	89.3
52.927	1.6251	30.7046	0.403	0°.535	98.6
53.529	2.5218	47.1109	0.618	0°.800	101.6
52.861	2.5907	49.0097	0.643	0°.840	100.6
52.927	2.7489	51.9376	0.681	0°.882	101.6

These results are analogous to those obtained with cadmium iodide. The molecular weight found is always higher than the normal, which is 76.2. The molecular weight is not a constant, but increases with the concentration. The molecules of ammonium sulphocyanate in acetone are, therefore, polymerized, the amount of polymerization increasing with the concentration, as is generally the case. As the dilution of the solution is increased the molecular complexes break down more and more into simple molecules, and at very great dilution it is probable that only a very few complex molecules would exist.

That solutions of ammonium sulphocyanate in acetone have some conductivity is shown by Laszczynski.[1] He gives the following results:

Ammonium sulphocyanate	v	1.45	2.90	5.8	11.6	23.2
	μ_v	14.6	16.3	18.5	21.6	25.6

The conductivity of this salt is larger than that of cadmium iodide, as would be expected. We have here also polymerization and dissociation in the same solution.

[1] Ztschr. Elektrochem., **2**, 56.

Molecular Weight of Mercuric Chloride in Acetone.

Two determinations were made at different dilutions, with the following results:

Acetone. Grams.	$HgCl_2$. Grams.	Grams $HgCl_2$ in 1000 grams acetone.	Conc. normal.	Rise in boiling-point.	Molecular weight.
53.320	5.953	111.647	0.412	0°.710	271.2
52.309	3.6554	69.881	0.258	0°.450	267.9

The molecular weight found agrees closely with that calculated for the formula $HgCl_2$, which is 271.2, and this value does not change appreciably with the dilution. It is obvious that the condition of this salt in solution is very different from the two already considered. There is no sign of polymerization of the molecules, and, consequently, no molecular complexes to break down as the dilution is increased. The molecules of mercuric chloride exist, then, in solution in acetone in the simplest possible state.

The question as to whether solutions of mercuric chloride in acetone conduct the current, is of special interest in the light of the above facts. It would be very remarkable, indeed, for a salt to give normal molecular weight which did not change with the dilution, and have any marked power of conducting the current.

We could say at once that it is highly improbable that mercuric chloride in acetone should have any considerable conductivity, since mercuric chloride in water—the strongest dissociating solvent—conducts to only a slight extent. But we are fortunate in having the data bearing upon this subject. Laszczynski[1] has measured the conductivity of mercuric chloride in acetone, and gives the following results:

Mercuric chloride	v	2.26	4.52	9.04	18.08	36.16
	μ_v	0.075	0.149	0.279	0.476	0.734

The conductivity is, thus, exceedingly small, just as would be expected.

Molecular Weight of Sodium Iodide in Acetone.

Five determinations of the molecular weight of sodium

[1] *Loc. cit.*

iodide in acetone, at very different dilutions, gave the following results:

Acetone. Grams.	NaI. Grams.	Grams NaI in 1000 grams acetone.	Conc. normal.	Rise in boiling-point.	Molecular weight.
51.876	0.921	17.754	0.118	0°.230	133.2
54.808	1.332	24.303	0.162	0°.304	137.9
51.287	1.5357	29.941	0.200	0°.371	139.2
55.088	2.0210	36.687	0.245	0°.440	143.8
51.876	2.3653	45.595	0.304	0°.550	143.0

The molecular weight of sodium iodide is not normal (149.9) at any of the dilutions employed. It is less than normal even in the most concentrated solution employed, and gradually diminishes as the dilution of the solution becomes greater and greater. This substance differs from the first two studied in that its molecular weight is always less than the normal, while in the cases of cadmium iodide and ammonium sulphocyanate the molecular weight found was always greater than the normal.

It is impossible to say at present what the conductivity of sodium iodide in acetone is, at the above dilutions. The conductivity of sodium iodide in acetone at much greater dilutions has been measured by Carrara.[1] It was found to be quite large, and increased rapidly with increase in dilution. At a volume of 256, the most concentrated solution whose conductivity was measured, the molecular conductivity is 126.3, while at a volume of 512, the molecular conductivity is 133.5. From these data the molecular conductivity at a volume of 10, would be somewhat less than 100. We propose to measure the conductivity of sodium iodide in acetone at greater concentrations, in connection with an investigation now in progress in this laboratory. For the present we can only say that it is very probable that sodium iodide also represents a condition in which there is both polymerization and dissociation.

It should be stated in connection with the work with sodium iodide, that the solutions in acetone were colored deeply yellow. I supposed at first that this was due to the liberation of iodine, but a test with starch paste showed that no free iodine

[1] Gazz. chim. ital., 27, I, 213.

was present. The yellow color may be due to some reaction between the acetone and sodium iodide, and I am inclined to lay less stress upon these results than upon those with the other three compounds.

I intended to determine also the molecular weight of lithium chloride in acetone, but found that it was not sufficiently soluble for the purpose.

Of the five substances which Dutoit and Friderich claim to give normal molecular weights in acetone, I have studied four, and find that only one gives any approach to normal values over a considerable range of dilution, and this one, mercuric chloride, has practically no conductivity. The fifth substance I could not investigate on account of its small solubility. These substances, instead of presenting any exception to the theory of electrolytic dissociation, fall directly in line with the theory, as so many similar cases have done. Indeed, it is extremely interesting to see how many apparent exceptions to the theory of electrolytic dissociation disappear as experimental methods become more refined, and experimental work more accurately carried out. The amount of evidence for the general correctness of this most fruitful generalization is at present so large that any apparent exception will be accepted only after it has been very thoroughly substantiated by repeated experiments. This should, however, not debar one from trying to discover exceptions, since there is more interest in one well-established exception than in many facts which could all have been predicted before any work was done.

Further work along the line indicated by this paper will be continued in this laboratory.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
MAY, 1901.

THE LOWERING OF THE FREEZING-POINT OF AQUEOUS HYDROGEN DIOXIDE.

BY HARRY C. JONES, JAMES BARNES, AND EDWARD P. HYDE.

A number of attempts have been made to find a solvent whose dissociating power was greater than that of water. A large number of solvents have been studied in this connection

with the result that of all the liquids investigated, water has the maximum ionizing power.

After examining all the work[1] which has been done it appeared to us not improbable that hydrogen dioxide might have a higher dissociating power than water. J. J. Thomson[2] pointed out some time ago that in terms of the theory of electrolytic dissociation a relation should exist between the dissociating power of solvents and their dielectric constants. A similar relation was recognized a little later by Nernst.[3] The dielectric constant of a mixture of hydrogen dioxide and water has been determined recently by Calvert.[4] From this he has calculated the dielectric constant of pure hydrogen dioxide to be 92.8 at 18°, while the dielectric constant of water at the same temperature is 81.

That hydrogen dioxide should have a high dissociating power was suspected by Brühl[5] a number of years ago. He regards the constitution of hydrogen dioxide to be

$$H-O\equiv O-H.$$

It is, therefore, in a high degree, an unsaturated compound, and since, according to Brühl, dissociating power depends upon the presence of tetravalent oxygen—upon the unsaturated condition—hydrogen dioxide should have a very high ionizing power. Brühl expressed the opinion that if the dissociating power of hydrogen dioxide could be measured it would probably be found to be greater than that of water.

We undertook this work with the hope of being able to determine, directly or indirectly, the dissociating power of hydrogen dioxide.

Purification of Hydrogen Dioxide.

We at first attempted to purify hydrogen dioxide by the method described by Bredig and von Berneck.[6] Marchand's commercial hydrogen dioxide was distilled on a water-bath

[1] A summary by H. C. Jones. This JOURNAL, **25**, 232.
[2] Phil. Mag., **36**, 320.
[3] Ztschr. phys. Chem., **13**, 531.
[4] Ann. der Phys., **1**, 483.
[5] Ber. d. chem. Ges., **28**, 2868.
[6] Ztschr. phys. Chem., **31**, 271.

under a pressure of about 80 mm. of mercury, until a very small residue remained. Pure barium hydroxide was added to the distillate until it was slightly alkaline, and then pure carbon dioxide was run into the solution to convert the excess of barium hydroxide into carbonate. The solution, after filtering, was distilled under diminished pressure, a slow current of air being allowed to flow through the liquid during the distillation. After about one-third of the liquid had distilled over, the remainder was filtered to remove the barium carbonate which had been formed from the acid barium carbonate in solution by boiling. The remainder of the solution was then distilled under diminished pressure, using a new distilling flask so as to avoid the presence of a scratched surface.

We found that during this process the loss of hydrogen dioxide by decomposition was very great. The acid barium carbonate is not all decomposed by boiling in the earlier stages of the distillation, but gradually separates out as the distillation proceeds. The decomposition of the dioxide, which takes place very rapidly in the later stages of the distillation, is probably caused by the solid barium carbonate which has separated, or by the acid carbonate still remaining in the solution. On account of the great loss of material we abandoned the above method in favor of the following, which we found to be far more satisfactory.

The commercial hydrogen dioxide was treated with zinc oxide and allowed to remain in contact with the oxide over night. By this means any hydrochloric or other volatile acid present was converted into the zinc salt. The solution was then filtered to remove the excess of zinc oxide, and distilled on a water-bath under a pressure of from 60 to 90 mm. of mercury. The distillation was allowed to proceed slowly, the temperature being kept as low as possible. The first third of the distillate was discarded since it contained comparatively little dioxide. The distillation was continued until only a few cubic centimeters remained in the flask. The last two-thirds of the distillate contained the material used in this work.

The advantage of this method over the one in which barium

hydroxide was employed, is probably to be found in the fact that the zinc chloride formed is so very soluble that it does not separate from the solution during the distillation until nearly all of the liquid has been distilled off. If an attempt is made to distil the last few drops out of the flask, a vigorous decomposition of the dioxide sets in, probably due to the separation from this concentrated solution of some solid material.

The aqueous solution of hydrogen dioxide thus purified was concentrated by placing it in a new and unscratched evaporating dish, which was very gently warmed on a water-bath. The temperature of the solution of hydrogen dioxide should not be allowed to rise above 50°, and it is better if the evaporation of water from the solution took place at a lower temperature, especially after the concentration of the solution has become considerable. We at first attempted to concentrate the solution of hydrogen dioxide by allowing its temperature to rise to 70° or 75°, as Wolfenstein[1] had done, taking the precaution recommended by him of allowing only a small part of the evaporating dish to come in contact with the water-bath. At these elevated temperatures the loss in hydrogen dioxide by decomposition was so great that much lower temperatures were employed.

An Attempt to Apply the Conductivity Method.

Having obtained pure hydrogen dioxide by the above method, in any quantity desired, we tried to determine the conductivity of solutions of salts in aqueous hydrogen dioxide. It was obvious at the outset that the ordinary platinum plates could not be used for electrodes, since the dioxide would be decomposed by them. We had our platinum electrodes very highly polished by a silversmith, and we worked at zero degrees. But even at this low temperature the dioxide was sufficiently decomposed by the metal to cover the plates with oxygen before a reading could be made. The aqueous solution of dioxide used contained only from 6 to 10 per cent, yet, even at such dilutions, the decomposition was sufficient to prevent us from measuring the conductivity of the solutions.

[1] Ber. d. chem. Ges., **28**, 3309.

We then tried a large number of other metals to see if one could be found which would not decompose the dioxide. All of the metals tried decomposed the hydrogen dioxide to such an extent that they could not be used for electrodes. We were therefore compelled to abandon the conductivity method (for the present) as a means of measuring the dissociation of electrolytes in aqueous hydrogen dioxide.

The only method at our disposal was that based upon the lowering of the freezing-point of solvents by dissolved substances.

Application of the Freezing-Point Method.

It seemed probable that by comparing the lowering of the freezing-point of aqueous hydrogen dioxide with the lowering of the freezing-point of water produced by the same substances, we could form some idea as to the relative dissociating power of water and of hydrogen dioxide. The lowering of the freezing-point of water produced by solutions of potassium chloride, potassium carbonate, and sodium carbonate of various dilutions, was studied in the usual manner. The solutions were prepared from pure, recrystallized salts, by dissolving weighed quantities in water, in calibrated measuring flasks. In every case the normal solution was prepared by weighing the salt, dissolving it and diluting to a known volume. The more dilute solutions were made from the normal solution by diluting measured volumes in measuring flasks.

The solutions in aqueous hydrogen dioxide were prepared in exactly the same manner. The normal solutions were made by dissolving weighed quantities of the salts in the dioxide, in a measuring flask, and diluting with the dioxide to the required volume. During the solution of the salt both the salt and solvent were kept at zero degrees by surrounding the flask with ice, in order that there might be no appreciable decomposition of the dioxide. The more dilute solutions were prepared from the normal solution by adding a measured volume of the latter to a 50 cc. measuring flask and diluting to volume with the solution of the dioxide. The solu-

tion of salt and the dioxide were, in all cases, kept at zero degrees.

We at first convinced ourselves that the lowering of the freezing-point of water by the dioxide was normal, *i. e.*, a gram-molecular normal solution of the dioxide froze 1°.86 lower than pure water. This is the same as to say that the molecular weight of hydrogen dioxide in water, as determined by the freezing-point method, corresponds to the formula H_2O_2. In determining the freezing-point of the aqueous hydrogen dioxide, the concentration of the dioxide is changed by the separation of ice. This was taken into account and the correction applied in the usual manner, by observing the amount which the solution was undercooled. In a similar manner the correction for change in concentration was applied when the freezing-point of the solution of salt was determined.

The following results were obtained for three salts in water, and in aqueous hydrogen dioxide of two concentrations.

Potassium Chloride in Water.

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	3°.416	3.416
0.75	2°.517	3.356
0.50	1°.684	3.368
0.25	0°.860	3.440
	Second Series.	
1.00	3°.411	3.411
0.75	2°.540	3.388
0.50	1°.700	3.400

Only two concentrations of potassium chloride in hydrogen dioxide were studied. The solvent contained 4.6 per cent of the dioxide. The following results were obtained:

Potassium Chloride in Aqueous Hydrogen Dioxide (4.6 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	3°.045	3.045
1.0	2°.995	2.995
0.5	1°.468	2.936
0.5	1°.460	2.920

These results show that the molecular depression of potassium chloride in aqueous hydrogen dioxide is much less than in water.

The following results were obtained with sodium nitrate:

Sodium Nitrate in Water.

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	3°.150	3.150
0.5	1°.621	3.242
0.25	0°.839	3.356

Sodium Nitrate in Aqueous Hydrogen Dioxide (4.6 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	3°.092	3.092
1.0	3°.095	3.095
0.5	1°.590	3.180
0.25	0°.808	3.232
	Second Series.	
1.0	3°.109	3.109
1.0	3°.110	3.110
0.5	1°.596	3.192

In the second series of experiments the solutions were prepared from entirely new material.

Sodium Nitrate in Stronger Hydrogen Dioxide (7 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	3°.042	3.042
0.5	1°.565	3.130
0.5	1°.571	3.142
0.25	0°.794	3.176

The results obtained with sodium nitrate in aqueous hydrogen dioxide, like those obtained with potassium chloride, are smaller than the corresponding results in water as the solvent. To test still further the effect of the hydrogen dioxide on the freezing-point lowering, a more concentrated solution of hydrogen dioxide in water was used. The lowerings obtained in the latter case were still smaller than when the more

dilute hydrogen dioxide was employed. We would have used solutions of hydrogen dioxide of greater concentration, but the freezing-point of such solutions would be so low that some refrigerating agent other than salt and ice would have to be employed; and it is difficult to regulate the temperatures of such very cold mixtures.

The results with potassium nitrate are even more striking than those with sodium nitrate. The freezing-point lowering of this salt in water, and in two solutions of hydrogen dioxide, was measured.

Potassium Nitrate in Water.

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	2°.656	2.656
0.75	2°.107	2.809
0.50	1°.470	2.940
0.25	0°.771	3.084

Potassium Nitrate in Aqueous Hydrogen Dioxide (5.3 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.00	2°.164	2.164
0.75	1°.667	2.223
0.50	1°.190	2.380
0.25	0°.627	2.508

Potassium Nitrate in Stronger Hydrogen Dioxide (7 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.00	1°.954	1.954
0.50	1°.057	2.114
0.25	0°.570	2.280

The lowering of the freezing-point of water by potassium nitrate is very much greater than the lowering of the freezing-point of aqueous hydrogen dioxide. The lowering becomes smaller, as we would expect, when the quantity of dioxide present is increased.

In all of these experiments the amount of the hydrogen dioxide present was determined after the salt had been intro-

duced, to see whether any appreciable decomposition of the dioxide had been effected by the salt. In no case was any appreciable change in the concentration of the dioxide detected.

The effect of the presence of hydrogen dioxide in water is, then, to diminish the lowering of the freezing-point produced by a dissolved salt. The question which naturally arises is, why is this the case? The simplest explanation seems to be that the hydrogen dioxide either decreases the dissociation which has been effected by the water, or acts as a polymerizing agent upon the undissociated molecules present in the solution.

In the case of potassium nitrate it is difficult to see how the results obtained can be accounted for on the basis of polymerization. Indeed, the decrease in the molecular lowering, produced by the presence of the hydrogen dioxide, is so great in this case that we would suspect some combination had taken place between the potassium nitrate and the hydrogen dioxide. This point we propose to investigate.

This is but a preliminary investigation. Further work on the lowering of the freezing-point of aqueous hydrogen dioxide will be done in this laboratory.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
February, 1901.

Several months after the above paper was written an account of an investigation on "Hydrogen Dioxide as an Acid," was presented to the German Electrochemical Society, by Bredig.[1] This has been recently described more fully by Calvert.[2]

Two facts brought out in this investigation are of special interest in this connection. It is shown that electrodes of iron covered with tin do not decompose dilute, alkaline, hydrogen dioxide, and can be used to measure the conductivity of such solutions. We shall try such electrodes in an extension of the above line of work.

[1] Ztschr. Elektrochem., 7, 622.
[2] Ztschr. phys. Chem., 38, 513.

It has also been shown by Calvert that a number of the strong alkalies can combine with hydrogen dioxide, forming definite compounds with it. This renders it not impossible that our suggestion that potassium nitrate may have combined with some of the hydrogen dioxide, is the true explanation of the results which we obtained. It at least makes it highly desirable that this point should be tested by direct experiment.

JOHNS HOPKINS UNIV.,
December, 1901.

A STUDY OF TRIBROMPHENOLBROMIDE.

BY J. H. KASTLE.

The compound called tribromphenolbromide was discovered by Benedikt in 1879.[1] He obtained it in the form of beautiful yellow crystals, which were found to melt at 118° C. On heating it to 125° C. it was found to decompose, evolving one atom of bromine, and giving an amorphous derivative which Benedikt called hexabromphenoquinone. Benedikt made the further interesting observation that on heating the compound under sulphuric acid it underwent a molecular rearrangement whereby it was transformed completely and quantitatively into tetrabromphenol. Benedikt further investigated the action of tribromphenolbromide on alcohol, tin and hydrochloric acid, aniline and phenol. In every case he obtained ordinary tribromphenol as a final product. He was therefore led to assign to the compound the following structural formula as that best comporting with the general behavior of the substance; *viz*:

$$C_6H_2Br_3(OBr).$$

In other words, he looked upon tribromphenolbromide as a derivative of tribromphenol in which the hydroxyl hydrogen of the latter had been replaced by bromine.

It seemed to the writer therefore to offer a fruitful field for further investigation, especially as the constitution of the compound, as determined by Benedikt, seemed to rest upon very

[1] Ann. Chem. (Liebig), 199, 127.

slender lines of evidence, and inasmuch further as no satisfactory explanation was offered for the remarkable molecular rearrangement which the compound undergoes under sulphuric acid. This investigation was begun in 1899. Unfortunately, it has been interrupted at various times by other work of a more pressing character, and is even yet incomplete. It is believed, however, that certain results already reached are of sufficient interest to warrant publication in their present form. The work has been done in collaboration with certain of the advanced students of the chemical department here, *viz.*, A. S. Loevenhart, Rosa Speyer, and J. W. Gilbert.

Preparation and Properties of Tribromphenolbromide. Conduct of Tribromphenolbromide towards Heat and Light. Action of Tribromphenolbromide on Water, Potassium Iodide, and Zinc Ethyl. Behavior of Tribromphenolbromide towards Bromine and Iodine.

By A. S. Loevenhart.

Tribromphenolbromide was prepared essentially according to Benedikt's method by adding an aqueous solution of phenol to one of bromine containing the bromine slightly in excess of the amount required. Usually a solution containing 4.7 grams of phenol was added to bromine water containing 13 cc. of bromine, and the mixture thoroughly shaken and allowed to stand for several hours. Under these conditions the tribromphenolbromide separates as a yellow granular precipitate, altogether different in appearance from tribromphenol. It has been found best to filter the substance through fine cotton cloth. After washing with water the compound was transferred to filter-paper and allowed to dry in the air, in the dark and at ordinary temperatures. Tribromphenolbromide is thus obtained in the form of a buff-colored powder. On analysis it was found to contain 19 per cent of easily replaceable bromine. As observed by Benedikt, the compound

can be obtained in beautiful crystalline condition by crystallizing from hot chloroform. On cooling, it separates from its solution in chloroform in the form of beautiful lemon-yellow plates or prisms melting at 118° C. Up to a certain limit the crystals become lighter in color the oftener the compound is recrystallized from chloroform. For reasons, to be discussed in a subsequent part of the paper, the compound is best preserved in open vessels and not in tightly stoppered bottles. The molecular weight of the compound was determined by the freezing-point method, using ethylene bromide as the solvent. An average of three concordant determinations gave 412.5 as the molecular weight. The calculated molecular weight of the compound is 410.

Conduct of Tribromphenolbromide Towards Heat and Light.

According to Benedikt, when tribromphenolbromide is heated it melts at 118° C. to a reddish liquid. If the temperature be raised to 125° C. the compound begins to decompose, evolving free bromine. If the compound be heated for some time at 130° C. in a current of carbon dioxide it loses 1 atom of bromine for each molecule of the compound decomposed, and there is left behind a reddish substance having much the appearance of molten sulphur. On dissolving this gummy mass in ether and adding alcohol to the solution a white amorphous substance is obtained, which, according to Benedikt, is hexabromphenoquinone,

$$C_6H_2Br_3O—OBr_3H_2C_6.$$

In the hope of throwing some further light on the constitution of this substance, and thereby learning something more of the nature of tribromphenolbromide itself, the attempt was made to synthesize hexabromphenoquinone from tribromphenolbromide and silver tribromphenolate in the following manner: Ten grams of finely powdered tribromphenolbromide were placed in a flask together with 30 cc. af chloroform and 10.5366 grams of silver tribromphenolate were added gradually. The reaction took place at once at ordinary temperatures, and after shaking thoroughly and standing for some time it was filtered from the silver bromide. The resi-

due was found to consist entirely of silver bromide. On the addition of alcohol to the filtrate it was found to yield a white flocculent precipitate, which proved to be identical in every respect with Benedikt's hexabromphenoquinone.

On the Action of Sunlight on Tribromphenolbromide in Solution in Carbon Bisulphide.

As already stated in the above, tribromphenolbromide in pure condition has, in the solid state, a beautiful yellow color. When dissolved in carbon bisulphide it imparts a yellow color to the solution, and if kept in the dark such solutions retain their yellow color unaltered for almost any length of time. Such solutions, however, have been found to change slowly, even in diffused light, and in the direct sunlight they rapidly assume the characteristic color of free bromine in solution in carbon bisulphide. Such having been found to be the case, it was decided to follow the decomposition in direct sunlight colorimetrically by comparing the solutions of tribromphenolbromide which had been exposed to the light for a given time with freshly prepared solutions of bromine in carbon bisulphide of known strength. A N/10 solution of tribromphenolbromide was made up in the dark and then exposed to direct sunlight, portions being removed from the flask from time to time for comparison with the standard solution of free bromine. The color comparisons were made in small Nessler cylinders of 30 cc. capacity and all having the same internal diameter. When the solution of tribromphenolbromide had become too deeply colored to make accurate comparisons possible, aliquot portions were removed from the flask and diluted to a given volume so as to get more accurate results. The color comparisons were always made on volumes of 10 cc. The following are the results obtained :

Time in minutes.	Percentage decomposition calculated for 1 atom of bromine.
32	67.90
45	84.87
57	113.25
67	141.51
84	181.20
99	181.20
140	201.60

From these colorimetric measurements it became evident that in the sunlight 2 atoms of bromine are liberated from each molecule of tribromphenolbromide, or that there is some other highly colored substance produced. In order to prove absolutely that it was free bromine which imparted the yellow color to the solution, 250 cc. of a N/10 solution of tribromphenolbromide in carbon bisulphide was prepared. This was exposed to the direct sunlight for six days. At the end of this time 10 cc. of the solution were removed from the flask and an excess of an aqueous solution of potassium iodide added. This was then titrated with decinormal thiosulphate. It required 16.45 cc. As the original solution fumed strongly in the air it was thought advisable to determine the total bromine by reducing with zinc dust and titrating with N/10 silver nitrate and ammonium sulphocyanate. It was found that each cubic centimeter of the solution contained 0.01468 gram of bromine in the form of free bromine and hydrobromic acid. Some of the original solution was now distilled at the lowest possible temperature. It was found that the distillate contained 0.01316 gram of free bromine and 0.00076 gram of bromine as hydrobromic acid per cubic centimeter. An equal amount of the bromine which went to form hydrobromic acid must have disappeared in the substitution. We have thus accounted for 0.01468 gram of bromine out of the 0.016 gram of bromine per cubic centimeter which should have been present in the solution if each molecule of tribromphenolbromine had liberated 2 atoms of bromine. The gummy mass left behind in the flask, after the distillation, was dissolved in chloroform and precipitated by the addition of alcohol. After several such precipitations it was obtained as a white, amorphous precipitate. A bromine determination was made on this compound with the following result :

	Calculated for $(C_6H_2Br_3O)_2$.	Found.
Br	64.00	64.46

In its physical properties this compound was found to be very similar to hexabromphenoquinone described in the above. Up to this time it has not been found possible to obtain it in

crystalline condition, and hence its constitution has not yet been settled definitely.

The Action of Water on Tribromphenolbromide.

In view of the ease with which tribromphenolbromide decomposes, both when heated in the solid state and in solution in organic solvents, it occurred to us that it might prove of interest to try its conduct towards water at high temperature. Accordingly, 5 grams of tribromphenolbromide were heated in a hard glass tube with 5 cc. of water, for ten hours, at 100° C. After a few minutes' heating on the water-bath the tube was observed to contain some bromine vapor, which, however, shortly disappeared. At the conclusion of the experiment the substance in the tube was found to be in a molten condition, but solidified on cooling. On opening the tube it was found that no pressure had developed. The supernatant liquid contained only a trace of bromine but was found to contain large quantities of hydrobromic acid. The solid mass was found to consist of a mixture of tribromphenol and tetrabromquinone. Hence the reaction must, in all probability, have taken place according to this equation:

$$3C_6H_2Br_3(OBr) + 2H_2O = 2C_6H_2Br_3(OH) + C_6Br_4O_2 + 2HBr + H_2O.$$

Action of Potassium Iodide on Tribromphenolbromide.

Tribromphenolbromide was found to be capable of setting free iodine from solutions of potassium iodide. It occurred to us, in this connection, that it might be possible to prepare tribromphenoliodide by means of this reaction. In order to test this point, 8 grams of tribromphenolbromide were ground to a fine powder and mixed with a slight excess of potassium iodide. The mass turned brown in color at once, indicating that the reaction between these two substances had begun even in the solid state. Before the reaction had proceeded far, however, 30 cc. of chloroform were added and the flask sealed and allowed to stand several days. On opening the flask it was found that the solution contained a large amount of free iodine, thereby indicating that the reaction had not oc-

curred in the manner hoped for. On adding alcohol to some of the solution obtained in the above, a precipitate of hexabromphenoquinone was obtained. The reaction of potassium iodide on tribromphenolbromide is therefore, in all probability, to be represented by the following equation:

$$2C_6H_2Br_3(OBr) + KI = C_6H_2Br_3O{-}OBr_3H_2C_6 + KBr + BrI.$$

It should be observed, however, that this reaction proceeds in this manner only in the absence of water, as may be seen from the following experiment: 0.205 gram of tribromphenolbromide were dissolved in 10 cc. of carbon bisulphide, and 25 cc. of water were added and an excess of potassium iodide. The free iodine was titrated with N/10 thiosulphate solution. The amount of thiosulphate solution required was found to vary between 9 and 10 cc., according to the relative amounts of water, carbon bisulphide, and potassium iodide present. Further, the supernatant aqueous solution gave, when acidified, a copious precipitate of tribromphenol. In aqueous solution, therefore, the action of potassium iodide on tribromphenolbromide takes place according to the following equations:

$$2C_6H_2Br_3(OBr) + 2KI = 2C_6H_3Br_3OK + Br_2 + I_2,$$

and $$Br_2 + 2KI = 2KBr + I_2.$$

This would account for the double amount of iodine set free. We see thus that tribromphenolbromide decomposes potassium iodide by virtue of the easily replaceable bromine which it contains, and also for the reason that it is an oxidizing agent. It will be observed, further, that in solution in organic solvents tribromphenolbromide tends toward the production of hexabromphenoquinone, whereas in aqueous solutions it tends towards the production of tribromphenol.

Action of Zinc Ethyl on Tribromphenolbromide.

If the constitution of tribromphenolbromide is correctly represented by Benedikt's formula, $C_6H_2Br_3(OBr)$, one would naturally expect to obtain ethyl tribromphenolate,

$$C_6H_2Br_3(OC_2H_5),$$

by treating it with zinc ethyl. In order to test this point,

equivalent quantities of tribromphenolbromide and zinc ethyl were brought together in absolute ether. A vigorous reaction occurred, but instead of obtaining ethyl tribromphenolate and zinc bromide, we obtained ethyl bromide and the zinc salt salt of tribromphenol. In other words, the reaction between these two substances occurs in a manner exactly the reverse of what one would naturally expect if Benedikt's view of the constitution of the compound is correct. The significance of this result will be discussed in a subsequent part of the paper.

Action of Iodine on Tribromphenolbromide.

In the hope of being able to prepare tribromphenoliodide it occurred to us to try the action of iodine on tribromphenolbromide. With this in view, 5 grams of tribromphenolbromide were dissolved in carbon bisulphide, and to this solution the calculated amount of iodine, 1.5 grams, was added and the solution well shaken. It soon became evident that some reaction had taken place, for the carbon bisulphide solution soon lost its violet color and assumed a brownish tint instead. After standing about two and a half hours the solution was distilled at the lowest possible temperature, the distillate showing the same brownish color as the solution itself. The distillate was tested both for bromine and iodine with the result that both were found to be present. The residue left in the distilling bulb was dissolved in chloroform and the solution precipitated with alcohol. The amorphous white precipitate thus obtained was shown to be hexabromphenoquinone. The action of iodine on tribromphenolbromide can therefore be represented by the following equation:

$$2C_6H_2Br_3(OBr) + I_2 = C_6H_2Br_2O{-}OBr_2H_2C_6 + 2BrI.$$

The Catalysis of Tribromphenolbromide by Bromine Vapor.

It was observed that tribromphenolbromide could not be preserved as well in tightly stoppered bottles as by freely exposing it to the air. This seemed to indicate that the traces of free bromine resulting from the slight decomposition of the compound at ordinary temperatures, if not removed, acted by

catalysis to greatly accelerate the decomposition of the rest of the compound. In order to test this point the following experiments were tried: Four tubes were prepared, each containing 0.5 gram of pure tribromphenolbromide. Into two of these, small amounts of bromine vapor were introduced. These tubes, together with the two containing no bromine, were then sealed. Two of the tubes, one containing bromine vapor and the other without, were kept in the dark for four days. A similar pair of tubes was exposed to the direct sunlight for eight hours. On examining the tubes that had been exposed to the direct sunlight, the next day, it could be easily seen that the greatest decomposition had occurred in the tubes containing the bromine vapor. The tubes were then opened and the vapor of bromine removed by a current of air. The material in the tubes was then carefully washed out with chloroform and an excess of an aqueous solution of potassium iodide added, and the free iodine titrated against N/10 thiosulphate solution. If none of the compound had decomposed, it would have required 24.4 cc. of thiosulphate. As a matter of fact, the tube containing the tribromphenolbromide without bromine required 22.65 cc. of the thiosulphate, corresponding to a decomposition of 7.13 per cent, while the tube containing the bromine vapor required only 17.65 cc., corresponding to a decomposition of 27.63 per cent. In other words, by means of a trace of bromine the decomposition of tribromphenolbromide had been accelerated nearly fourfold. The second pair of tubes was allowed to remain in the dark four days, when they were opened and the bromine vapor removed by a current of air. The residues were titrated with sodium thiosulphate after the addition of potassium iodide. The tube which did not contain bromine vapor originally, required 23.47 cc. of thiosulphate, corresponding to a decomposition of 3.77 per cent, while the tube containing the bromine vapor originally, required 16.95 cc. of thiosulphate, corresponding to a decomposition of 30.5 per cent. In this case the decomposition of tribromphenolbromide had taken place eight times faster in the presence of bromine than without. The great acceleration of the decomposition of this compound

by a small amount of bromine vapor is a very remarkable and noteworthy fact.

The Constitution of Tribromphenolbromide. The Preparation and Properties of Tribromphenylsulphonate. The Conversion of Tribromphenolbromide into Metadibromquinone.

By Rosa Speyer.

After some time the investigation of tribromphenolbromide was resumed at this point, for the reason that the constitution of the compound could not yet be looked upon as definitely settled either in favor of or against Benedikt's view. The peculiar conduct of the compound towards zinc ethyl, as pointed out in the preceding paper, still left the matter in doubt, although the formation of zinc salt of tribromphenol rather than its ethyl ether would seem to indicate that Benedikt's formula is incorrect, and that tribromphenolbromide is by no means as simple as he represented it to be. In order to throw further light upon this subject, it occurred to us that it might be well to attempt the preparation of the tribromphenyl ether of benzenesulphonic acid by two distinct methods, the first being by the action of benzenesulphonchloride on sodium tribromphenolate; the second being by the action of sodium benzenesulphinate on tribromphenolbromide. Should both of these reactions yield the same sulphonic ether, it would probably be regarded as tolerably certain proof of the correctness of Benedikt's formula for this compound.

Tribromphenyl Benzenesulphonate,

$C_6H_5SO_2.OC_6H_2Br_3$.

This ether is readily prepared by the action of sodium tribromphenolate on benzenesulphonchloride. The sulphonchloride is dissolved in absolute ether, and to this solution finely powdered anhydrous sodium tribromphenolate was added, in small quantities at a time and with constant shaking, until a considerable excess had been added. The solution was then filtered and the clear filtrate allowed to evap-

orate spontaneously at ordinary temperature, when the sulphonic ether was obtained. A still better method for the preparation of the ether is the following: The sodium salt of tribromphenol is dissolved in absolute alcohol, and to this solution there is added the theoretical quantity of benzenesulphonchloride and the solution heated to boiling. On filtering from the sodium chloride and cooling, the sulphonic ether crystallizes out. It may be purified by dissolving in alcohol and treating with animal charcoal. The ether crystallizes from alcohol in the form of colorless, glistening, rhombic plates. It melts at 99° C. (uncorr.) It is insoluble in water and cold alcohol. It is readily soluble, however, in hot alcohol, benzene, carbon bisulphide, acetone, and ethyl ether. From hot concentrated solutions in alcohol it frequently separates as an oil which solidifies, on cooling, to a white crystalline mass. The nature of the compound thus obtained was was determined by saponification with alcoholic caustic soda. To saponify 0.2353 gram of the ether, 5 cc. of N/10 caustic soda were required. Theory for $C_6H_5SO_2.OC_6H_2Br_3$, 5 cc. N/10 NaOH.

Unlike most of the sulphonic ethers, known to us at present, this compound has been found to be remarkably stable towards water and other hydrolyzing agents.

Action of Sodium Benzenesulphinate on Tribromphenolbromide.

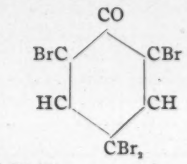
In order to determine whether tribromphenyl benzenesulphonate could be formed from tribromphenolbromide, a quantity of benzenesulphinic acid was prepared by Gattermann's method and converted into the sodium salt. A small quantity of tribromphenolbromide was then dissolved in carbon bisulphide, and to this solution the theoretical amount of finely powdered sodium benzenesulphinate was added, and the mixture thoroughly shaken. After standing for an hour the solution was filtered. The white residue was found to consist of sodium bromide. On allowing the filtrate to evaporate spontaneously, a reddish gummy substance was obtained, together with a smaller quantity of an oily product having the characteristic odor of a sulphonchloride or bromide. The

gummy substance was identified as Benedikt's hexabromphenoquinone. Hence the reaction between the sodium benzenesulphinate and tribromphenolbromide does not result in the formation of a sulphonic ether but takes place in the sense of this equation:

$$2C_6H_2Br_4O + C_6H_5SO_2Na = (C_6H_2Br_3O)_2 + NaBr + C_6H_5SO_2Br.$$

Action of Silver Nitrate on Tribromphenolbromide.

Beyond proving the incorrectness of Benedikt's formula for tribromphenolbromide, but little tangible evidence of the real nature of the compound has been obtained up to this time. It occurred to us in this connection, however, to test the conduct of silver nitrate towards tribromphenolbromide. On boiling a solution of silver nitrate, to which some tribromphenolbromide had been added, it was observed that a crystalline precipitate was thrown down. This was filtered off and purified by dissolving in alcohol and reprecipitating with water, when the substance was obtained in the form of yellow iridescent laminae. The compound was still further purified by sublimation. It was observed to melt at 131° C. The compound was identified as metadibromquinone by comparing it with some of this compound prepared by the method of Levy and Schultz.[1] About the time this observation was made, Thiele and Eichwede[2] also obtained metadibromquinone from tribromphenolbromide by treating the latter substance in acetic acid solution with lead acetate. These observers came to the conclusion, therefore, that tribromphenolbromide has a quinone structure, and that its chemical behavior can best be interpreted by the following graphic formula:



[1] Ann. Chem. (Liebig), 210, 159.
[2] Ber. d. chem. Ges., 33, 673 (1900).

In view of the simple relation existing between tribromphenolbromide and metadibromquinone, it would seem possible to pass from the one of these substances to the other by a number of simple reagents, such as silver oxide, calcium carbonate, etc. This, however, has not been our experience, possibly for the reason that the proper solvent was not employed. Of all the reagents thus far tried, fuming nitric acid has been found to give the largest yield of metadibromquinone from tribromphenolbromide.

On the Molecular Rearrangement of Tribromphenolbromide by Means of Sulphuric Acid.

By J. W. Gilbert.

As already stated above, the most interesting property of tribromphenolbromide is that when heated to 118° C., under sulphuric acid, it undergoes a molecular rearrangement whereby it is transformed completely into tetrabromphenol. This remarkable molecular rearrangement was first described by Benedikt, who pictured the change as occurring in this manner:

$$\begin{matrix} C_6H & H & Br_2O & Br \\ & Br & OBr_2 & H \end{matrix} \quad HC_6 = 2C_6HBr_4OH.$$

Obviously this explanation is by means satisfactory, since it entirely ignores the part played by the sulphuric acid, and since, further, the rearrangement in question cannot be brought about by heat alone. A further study of this molecular rearrangement was therefore undertaken in the hope of being able to determine the part played by the sulphuric acid in the change. On heating tribromphenolbromide under sulphuric acid, as directed by Benedikt, it was observed that the substance melted under the sulphuric acid at 113° C. It was thought from this, therefore, that possibly the sulphuric acid could bring about the change in question without the aid of heat.

With the view of testing this point some finely powdered

tribromphenolbromide was mixed with concentrated sulphuric acid at ordinary temperature. It was observed that the compound underwent a change of color and gradually became perfectly white. The acid was then poured off and the compound washed with water and purified by crystallizing from alcohol to which an equal volume of boiling water had been added. The substance was finally obtained in the form of white, felt-like needles, which were found to melt at 109° C. This compound is tetrabromphenol, and the fact that it is formed under these circumstances certainly goes to show that the molecular rearrangement of tribromphenolbromide is due to the sulphuric acid and not to an elevation of temperature. In order to determine whether the molecular rearrangement could be brought about by other substances, the conduct of tribromphenolbromide was tried towards the following reagents: Paraffine, dibrombenzene, glycerine, concentrated hydrochloric acid, glacial acetic acid, dilute sulphuric acid, benzenesulphonchloride, benzenesulphonic acid, a saturated solution of iodic acid, sodium acid sulphite, carbon tetrachloride, potassium bromide, and potassium chloride.

Nearly all of these substances were found to decompose tribromphenolbromide, especially at high temperatures, but in no case was the molecular rearrangement brought about.

That it is not due to acids in general may be seen from the following: A quantity of tribromphenolbromide was allowed to stand for one week under concentrated hydrobromic acid. At the end of this time the compound was found to have lost its color and to have become white. The substance was filtered from the hydrobromic acid, washed with water, and recrystallized. It was found to melt at 91° C. and was found to be identical in every respect with tribromphenol. That undissociated acids in general do not bring about the molecular rearrangement was proved by dissolving tribromphenolbromide in a concentrated solution of hydrochloric acid in chloroform. Some of this solution was heated in sealed tubes, after which the chloroform was allowed to evaporate off, when tribromphenolbromide was obtained in unaltered condition.

These results leave practically no room for doubt that the

molecular rearrangement of tribromphenolbromide is accomplished solely by the action of concentrated sulphuric acid.

Trichlorphenolbromide.

In this connection, however, it should be noted that it is stated in Watts' "Chemical Dictionary" and Beilstein's "Organische Chemie," that trichlorphenolbromide, an analogous compound, is transformed by heating under water into an isomer, probably trichlormonobromphenol. In view, therefore, of what had been observed concerning the molecular rearrangement of tribromphenolbromide it was thought advisable to repeat this experiment.

Accordingly, trichlorphenolbromide was prepared in the following manner: Trichlorphenol was converted into the sodium salt by treating with the required amount of caustic soda. Five grams of the sodium salt thus obtained were dissolved in 500 cc. of water. To this solution 3 cc. of concentrated hydrobromic acid were added. The pasty mass thus obtained was immediately poured into a saturated solution of bromine containg 5 cc. of bromine. The mixed solution was thoroughly shaken and allowed to stand for some time. Trichlorphenolbromide separated from this solution in the form of a light-yellow, granular precipitate, altogether similar in appearance to tribromphenolbromide. The compound was purified by crystallizing from hot chloroform. In pure condition it was found to melt at 97° C. Like tribromphenolbromide, this substance is lemon-yellow in color but more soluble in chloroform than the former. The amount of easily replaceable bromine in trichlorphenolbromide was determined by reducing it with sodium acid sulphite and titrating with N/10 silver nitrate. 0.2 gram of the compound was taken for analysis.

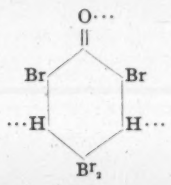
	Calculated for Trichlorphenolbromide.	Found.
Br	0.577	0.564

Some of this compound, when ground to a fine powder and melted under water, was found to decompose with evolution of bromine. It was not transformed, however, into the isomeric

trichlormonobromphenol. On the other hand, trichlorphenolbromide is readily transformed by sulphuric acid into trichlormonobromphenol. In order to show this, 0.5 gram of trichlorphenolbromide was heated under sulphuric acid. On cooling, the acid was poured off and the residue washed with water. The residual acid and washings were tested for bromine with silver nitrate with negative result. The trichlormonobromphenol formed in this experiment was found to weigh, when air-dried, 0.508 gram. It will be observed, therefore, that it is the sulphuric acid and not the water which effects the conversion of trichlorphenolbromide into trichlormonobromphenol.

In view of these results, therefore, there can be no doubt that the conversion of tribromphenolbromide into tetrabromphenol is brought about by means of concentrated sulphuric acid.

The question naturally presents itself, how can sulphuric acid accomplish this change? In answer to this the following explanation has suggested itself in the light of Thiele and Eichwede's formula for tribromphenolbromide, which, in view of the former's[1] ideas of partial valence, may be written as follows:

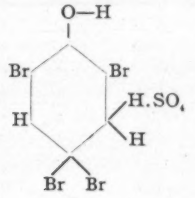


I.

From what we know of the manner in which sulphuric acid dissociates as an electrolyte, it would seem probable, at least, that in its action on tribromphenolbromide the hydrogen ion would add itself to the quinone oxygen of the compound, thereby converting it into a phenol hydroxyl group. The

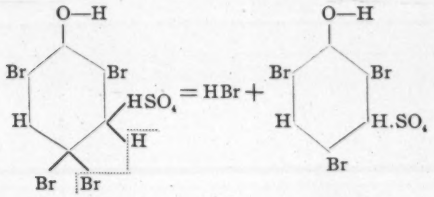
[1] Thiele: Zur Kentniss der ungesättigten Verbindungen. Ann. Chem. (Liebig), 306, 129.

HSO_4 ion could then unite with either of the unsaturated groups in the meta position in the ring. This change may be represented graphically as follows:



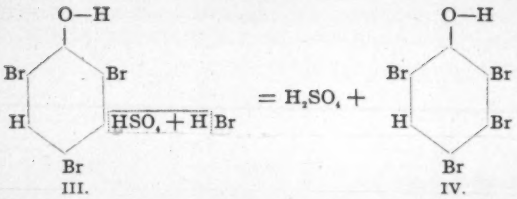
II.

If now, from compound II, hydrobromic acid were to be split off, and there is every reason for supposing that such a decomposition might occur, there would remain a compound having the nature of an acid ester sulphate, thus:

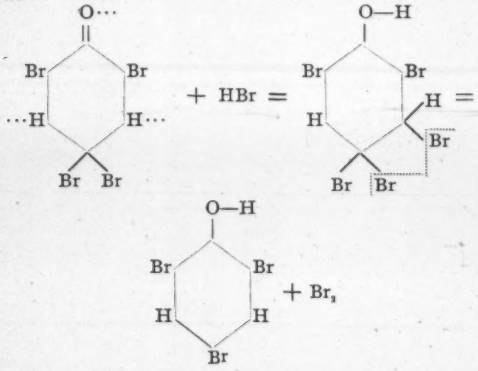


III.

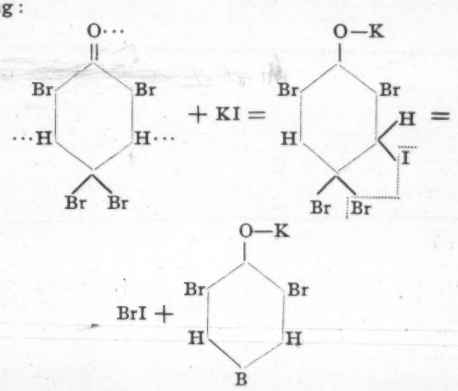
From what we know of the ease with which acid ethyl sulphate, $C_2H_5HSO_4$, is decomposed by hydrobromic acid to form ethyl bromide and sulphuric acid, it would seem logical to suppose that the hydrobromic acid resulting from the decomposition of compound II. would at once act upon compound III., with the production of tetrabromphenol and sulphuric acid, thus:



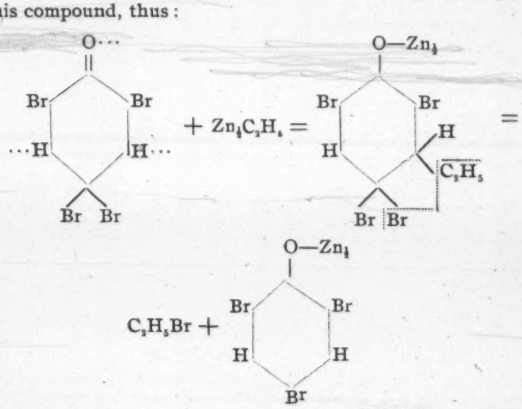
It will be observed that, like many other catalytic processes, the change in question is of a cyclical character. It is believed, further, that all changes brought about by electrolytes on tribromphenolbromide can be explained by the supposition that the hydrogen or positive ion enters into combination with the quinone oxygen of the compound, thereby converting it into a phenol or one of its salts. The negative ion probably enters into combination with one of the meta groups in the ring, and finally, as the result of cleavages occurring between the atoms or groups in the meta and para positions, the end products of the reaction are produced. For example, as shown in the above, tribromphenolbromide is reduced to tribromphenol by means of hydrobromic acid. It is believed that the changes taking place can be represented as follows :



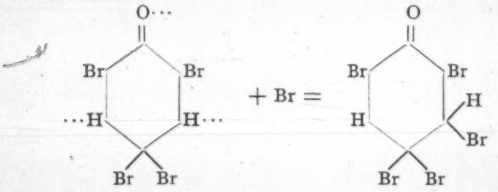
In the same way we can explain the action of potassium iodide on tribromphenolbromide, as may be seen from the following:



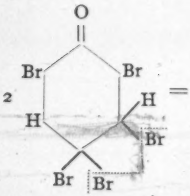
and, similarly, we can account for the action of zinc ethyl on this compound, thus:

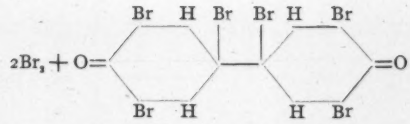


On the other hand, with electronegative elements such as bromine and iodine, which, as we have seen, also decompose tribromphenolbromide, and which have little or no affinity for the quinone oxygen, the case is somewhat different. Here the addition probably takes place on one of the groups in the meta position in the ring, with the production of an unstable intermediate product which, as the result of secondary changes occurring between the atoms or groups in the meta and para positions, gives the final products of the decomposition.[1] Thus, in the catalysis of tribromphenolbromide by means of bromine vapor, we probably have the following changes occurring :



and



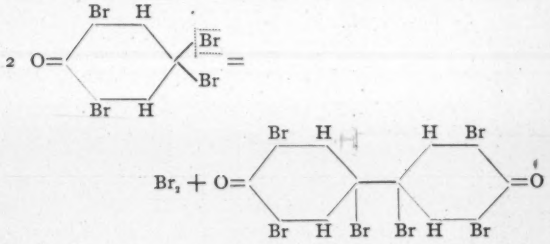


and, inasmuch as more and more bromine is produced the longer the reaction proceeds, we can readily understand how

[1] Thiele : Zur Kentniss der ungesättigten Verbindungen. Ann. Chem. (Liebig), 306, 133.

a mere trace of bromine is all that is needed to start the decomposition. A similar explanation holds for the action of iodine upon tribromphenolbromide in solution. Finally, it should be observed that the quinone formula for tribromphenolbromide enables us to account satisfactorily for the decomposition of tribromphenolbromide by heat, whereby 1 atom of bromine is evolved from each molecule of the compound undergoing decomposition. The fact that two of the bromine atoms in this derivative are in combination with the same carbon atom indicates that in tribromphenolbromide we have to do with essentially the same sort of instability that is met with in the hexabrom addition-product of benzene itself, and it will be recalled that in this compound one of the atoms is readily lost from each carbon atom.

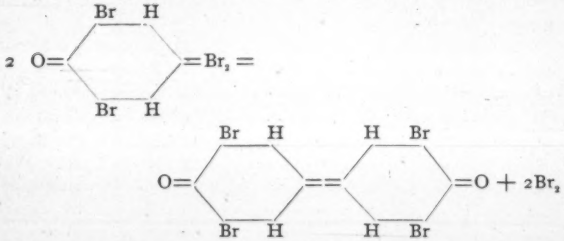
Further, if 1 atom of bromine is given up by the molecule of tribromphenolbromide, an unsaturated residue is left, two of which would in all probability unite to form Benedikt's hexabromphenoquinone. It follows further, from the above considerations, that the two quinone residues in hexabromphenoquinone are not united through the oxygen atoms, as was supposed by Benedikt, but rather through the para-carbon atoms. Thus the decomposition of tribromphenolbromide by heat may be represented as follows:



The formation of hexabromphenoquinone from tribromphenolbromide is certainly one of the most characteristic properties of the latter substance. On account of its amorphous character, however, and its great stability, but little is known of its chemical nature, and further work is necessary for a

clear understanding of this compound and its relation to tribromphenolbromide.

The loss of 2 atoms of bromine from the compound, which occurs on the exposure of a carbon bisulphide solution of tribromphenolbromide to light, is much more difficult to explain. Here also the product of the reaction is amorphous and exceedingly stable, and in fact shows many points of resemblance to hexabromphenoquinone. Like this compound, it probably contains two benzene residues, and tentatively, at least, we may represent its formation in the following manner:



A further study of this compound is necessary, however, to a better understanding of the decomposition of tribromphenolbromide by light.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KY., July, 1901.

SOLUBILITY OF MIXTURES OF SODIUM SULPHATE AND SODIUM CHLORIDE.[1]

BY ATHERTON SEIDELL.

The solubility in water of mixtures of several pairs of electrolytes, in which one member of the pair is relatively much less soluble than the other, has lately been investigated in this laboratory by Dr. Frank K. Cameron and the author.[2] In connection with this work, the results presented in this paper were obtained, on mixtures of a pair of salts yielding a common ion, presumably, and having the additional feature that

[1] Published by permission of the Secretary of Agriculture.

[2] Solution studies of salts occurring in alkali soils, Bulletin 18, Division of Soils, U. S. Department of Agriculture.

both members of the pair are readily soluble. A good deal of work of this description has been done in recent years, but so far as I am aware, this pair of salts has not previously commended itself to investigators, owing probably to the well-known tendency of sodium sulphate and its hydrates to form supersaturated solutions, which are difficult to handle; and to the further fact, that salts which separate in the solid phase without water of crystallization, have hitherto appealed to investigators on account of the readiness with which the total amount of salt in solution may be determined by evaporation and drying, thus affording obvious analytical advantages in dealing with them.

In a few instances more than one investigator has worked with the same pair of salts, but a comparison of the results obtained was not possible, since the results were expressed in the one case in terms of grams of salts dissolved in a given weight of solvent, and in the other in terms of the grams of salts dissolved in a given volume of solution, and since the weights of the solutions were not given, there is no satisfactory way by which the results may be calculated to the same basis.

A recognition of the above fact is very important in all such work upon mutual solubility effects, and in order that the results may be of the greatest usefulness they should be presented in both ways.

EXPERIMENTAL WORK.

Before proceeding to a discussion of the results, a short description will be given of the manner in which the experimental work was carried on. In the majority of cases studied by other investigators, the salts with which they worked are such as crystallize without water of crystallization; hence it was possible for these investigators to make determinations of the total grams of salts in solutions by evaporation, and then by a determination of one of the constituents to obtain the other by difference. In the case under consideration, however, it was found necessary to make the determination of each of the salts in the weighed portion of the solution. The sodium chloride was determined by calculating from the re-

sults of titrations with N/10 solution of silver nitrate; and the sodium sulphate by calculating from the grams of barium sulphate, obtained by precipitation in the usual way.

The series of solutions were made up in bottles and so prepared that the amount of sodium sulphate should be in excess in the bottles with the lower numbers, the amount of sodium chloride gradually increasing from the second bottle on. In the bottles with the higher numbers the sodium chloride was in excess, and the amount of sodium sulphate gradually diminished. The first bottle contained only sodium sulphate in solution, the last only sodium chloride. Care was exercised in the determinations made at the several temperatures to have more than one bottle containing both salts present as solid phases in order that the point of intersection of the two curves representing the solubility of each salt in solutions of the other should be accurately determined. The bottles thus prepared and stoppered tightly were placed in a constant-temperature water-bath, in which they were rotated in a manner causing thorough agitation of the solutions for periods of eighteen to twenty-four hours. After the period of agitation the bottles were allowed to remain upright in the bath long enough for the solid material to subside and leave the supernatant solution clear. A 50 cc. portion of each solution was withdrawn by means of a pipette and transferred to a weighing-bottle and the weight of the solution taken. This amount of solution was then washed into a larger graduated flask, and, after diluting sufficiently, aliquot portions were taken for analysis as already described.

The results of the analyses at the various temperatures are given in the accompanying tables. In each case the weights of a given volume of the solutions are given in the first column. The grams of NaCl and Na_2SO_4 present in this volume are given in the second and third columns. The grams of sodium chloride and sodium sulphate present in 100 grams of water are given in the fourth and fifth columns, and finally the gram-molecules of sodium chloride and sodium sulphate per liter of solution are given in the sixth and seventh columns. The curves plotted in the diagram are on the basis of the results given in the fourth and fifth columns, giving the

grams of each salt present in 100 grams of water at the various temperatures. These figures were selected simply because they yield a diagram which is not so crowded, and is, therefore, clearer than if the results were plotted on any other basis. The nature of the curves is in no wise different, and the peculiarities they present are as clearly seen as they would be if plotted on any other basis.

Table I.—Temperature 10° C.

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. solution.	Grams Na_2SO_4 per 100 cc. solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
107.98	0.00	9.04	0.00	9.14	0.000	0.641
108.28	4.19	6.28	4.28	6.42	0.722	0.445
110.18	9.25	4.59	9.60	4.76	1.593	0.325
114.98	15.04	3.83	15.65	3.99	2.590	0.271
116.38	20.16	3.67	21.82	3.97	3.473	0.260
119.23	24.89	3.75	28.13	4.15	4.288	0.266
120.72	27.04	3.89	30.11	4.34	4.552	0.276
121.73	28.70	4.08	32.27	4.59	4.944	0.289
122.34	29.82	4.19	33.76	4.75	5.137	0.297

Table II.—Temperature 21°.5 C.

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na_2SO_4 per 100 cc. of solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
116.37	0.00	20.46	0.00	21.33	0.000	1.450
116.95	8.51	14.54	9.05	15.48	1.465	1.030
119.85	15.96	12.54	17.48	13.73	2.750	0.889
121.41	18.49	12.34	20.41	13.62	3.185	0.875
124.34	22.93	13.27	26.01	15.05	3.950	0.941
124.37	23.40	12.74	26.53	14.44	4.031	0.903
124.43	24.46	11.80	27.74	13.39	4.214	0.836
124.35	27.39	9.33	31.25	10.64	4.719	0.661
124.34	27.83	8.99	31.80	10.28	4.794	0.637
123.48	28.21	7.41	32.10	8.43	4.860	0.525
121.86	29.66	4.16	33.69	4.73	5.110	0.295
121.20	30.18	2.45	34.08	2.77	5.199	0.174
119.72	31.34	0.00	35.46	0.00	5.399	0.000

Table III.—Temperature 25° C.

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na_2SO_4 per 100 cc. of solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
121.56	0.00	27.14	0.00	28.74	0.000	1.923
121.16	2.56	24.87	2.74	26.57	0.442	1.764
121.76	7.56	21.47	8.15	23.15	1.301	1.522
....	16.90	19.15	....	....	2.912	1.357
124.94	17.76	18.35	19.86	20.52	3.060	1.301
124.05	22.52	13.13	25.48	14.86	3.880	0.931
123.89	27.39	8.73	31.21	9.95	4.719	0.619
123.79	27.98	8.40	32.02	9.61	4.820	0.595

Table IV.—Temperature 27° C.

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na_2SO_4 per 100 cc. of solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
122.79	0.00	29.13	0.00	31.10	0.000	2.065
123.04	2.49	26.90	2.66	28.73	0.430	1.906
122.98	4.91	25.23	5.29	27.17	0.846	1.788
123.49	7.28	24.00	7.90	26.02	1.255	1.701
125.88	14.40	22.18	16.13	24.83	2.480	1.571
125.34	16.90	19.12	18.91	21.39	2.912	1.355
124.89	17.56	17.97	19.64	20.11	3.025	1.274
124.46	18.46	17.14	20.77	19.29	3.180	1.214
123.80	28.22	8.32	32.33	9.53	4.861	0.590

Table V.—Temperature 30° C.

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. solution.	Grams Na_2SO_4 per 100 cc. solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
128.09	0.00	36.41	0.00	39.70	0.000	2.580
128.16	2.23	34.84	2.45	38.25	0.384	2.469
128.44	5.07	32.98	5.61	36.50	0.873	2.337
129.02	7.09	32.25	7.91	35.96	1.221	2.287
127.63	9.52	28.39	10.61	31.64	1.640	2.017
127.03	11.04	26.68	12.36	29.87	1.901	1.891
125.76	13.99	22.37	15.65	25.02	2.411	1.586
124.90	16.48	19.04	18.44	21.30	2.839	1.350
124.39	18.40	16.97	20.66	19.06	3.170	1.203
123.58	28.32	7.91	32.43	9.06	4.878	0.561

Table VI.—Temperature 33° C.

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na_2SO_4 per 100 cc. of solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
132.89	0.00	43.38	0.00	48.48	0.000	3.075
132.30	1.09	41.64	1.22	46.49	0.188	2.951
131.78	1.79	40.44	1.99	45.16	0.308	2.866
131.47	2.37	39.50	2.64	44.09	0.408	2.800
130.86	3.11	38.17	3.47	42.61	0.536	2.705
126.50	10.86	26.21	12.14	29.32	1.871	1.858
123.68	19.45	15.31	21.87	16.83	3.351	1.085
123.42	28.62	7.64	32.84	8.76	4.930	0.541
121.68	29.84	4.07	33.99	4.63	5.140	0.288
120.80	30.54	2.41	34.77	2.75	5.261	0.171

Table VII.—Temperature 35° C.

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na_2SO_4 per 100 cc. of solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
132.36	0.00	42.89	0.00	47.94	0.000	3.040
131.37	1.93	39.39	2.14	43.75	0.333	2.792
125.61	12.19	23.59	13.57	26.26	2.099	1.711
123.77	16.78	17.64	18.78	19.74	2.891	1.250
123.08	28.47	7.39	31.91	8.28	4.905	0.524
119.30	31.34	0.00	35.63	0.00	5.399	0.000

DISCUSSION OF RESULTS.

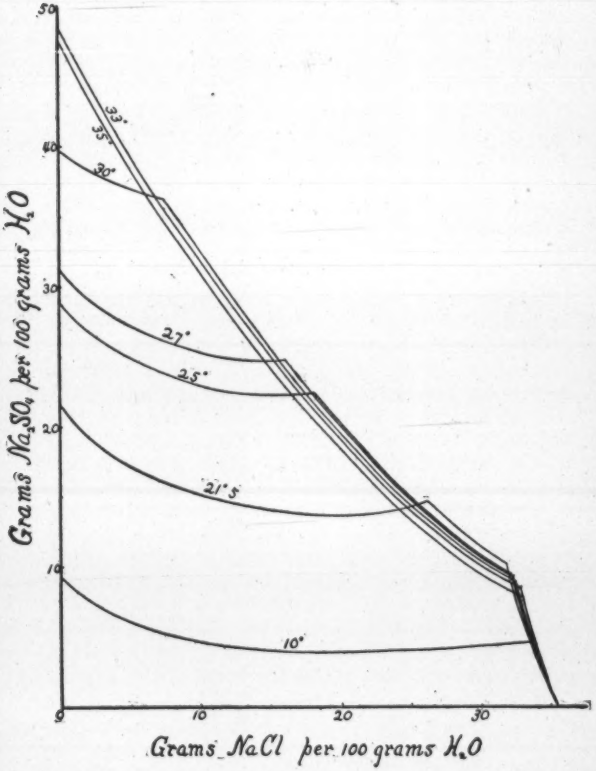
From Mulder's[1] results on the solubility of sodium sulphate, quoted in Comey's "Dictionary of Solubilities," page 452, it appears that the figure given for the solubility of sodium sulphate at 21°.5 is somewhat too low. Mulder found that at 21°.5 C. there was contained 21.7 parts of sodium sulphate per 100 parts water, while the results here show only 21.33 parts. This difference is possibly due to an error in the temperature observation in the present case. It appears that at 21°.3 C. Mulder obtains the same figures that are given here for 21°.5, consequently it may well be that the temperature at which the work here described was done may have been 21°.3 instead of 21°.5. The thermometer used was graduated only to whole degrees, and moreover had not been calibrated, so that such an error might easily be thus accounted for. Similarly, for the results obtained at other temperatures, a correction may be applied by comparing with Mulder's results, and there would be obtained 25°.4 instead of 25° C., 26°.5 instead of 27°, 29°.6 instead of 30°, 32°.25 instead of 33°. For 35°, however, a similar correction cannot well be allowed, since Mulder finds for 35°, 50.2 parts dissolved against only 47.9 in the present case.

An inspection of the diagram will show that there are present two distinct classes of curves, one class representing re-

[1] "Scheikundige Verhandelingen Onderzoekingen," edited by Mulder, Rotterdam, 1857-64. The original is not accessible to me.

sults obtained above 33° C., consisting of pairs of curves with one intersection as required by the phase rule; the other class representing results obtained at temperatures below 33°, showing three curves in each case, with two points of intersection.

To account for the peculiarity in the nature of the curve



representing the mutual solubility of these two salts in solutions of each other, it is necessary to remember the peculiarity exhibited by sodium sulphate in regard to its solubility alone in water at various temperatures. It is well known that at about 33° sodium sulphate changes from its characteristic ten hydrate crystalline form to the anhydrous salt. Consequently at this temperature, and above, the curves represent the solubilties of two, simple, non-isomorphous, anhydrous salts, sodium sulphate and sodium chloride, with one homogeneous solid phase, except at one point, the point of intersection. This behavior is in strict accord with the phase rule, and the cases described here appear to be perfectly normal.

Below 33°, however, a different state of affairs exists, as will be seen by referring to the diagram. The solubilities of various mixtures for any given temperature below 33° and above a temperature in the neighborhood of 17° C. are seen to be expressed by *three* curves intersecting in *two* points.

The lowest curve representing the solutions in which sodium chloride is present in excess, lie close to, and present the same general features as those curves representing the same mixtures at higher temperatures. The middle curve in each case is practically parallel to the curves obtained at higher temperatures when the solutions were in contact with solid anhydrous sodium sulphate. And, as will be presently pointed out, the solid phase controlling these middle curves is in fact the anhydrous salt, notwithstanding that they represent conditions existing below 33°.

The upper curve is the normal solubility curve for the decahydrate of sodium sulphate in solutions of sodium chloride. As will be seen from the diagram, the general nature of the solubility curve for the decahydrate is quite different from that for the anhydrous salts. And, certainly, at the lower temperatures it presents the unusual feature of a minimum point. At a temperature below 17°, the solid phase in contact with the solution is probably the heptahydrate. One curve, for 10° C., was determined, and as the diagram shows, it is entirely similar to the solubility curve for the decahydrate.

Considering further the course of the curves obtained at

temperatures below 33°, it is seen that in each case as the original direction of these curves causes them to come into the region of the curves for anhydrous salt (that is, the curves for 33° and above), the direction of the former is changed and becomes parallel to the latter curves, itself a strong argument for the view that the solid phase in contact with the solution was the same in all such cases, *i. e.*, the anhydrous sodium sulphate. If the curves for the decahydrate continued their direction, and crossed the curves for the anhydrous salt in order to meet the line representing the solubility of sodium chloride in sodium sulphate extended, it would mean that solutions would be obtained which would be supersaturated with respect to the anhydrous sodium sulphate. In order that the solution could have been supersaturated with respect to anhydrous sodium sulphate, it would be necessary that none of the solid anhydrous salt should be in contact with the solution. The temperature being below 33° would ordinarily insure the presence of no anhydrous sodium sulphate, consequently it is to be expected that such points in the field beyond the 33° curve should be obtained. In no case, however, were they realized, and we are again led to the conclusion that anhydrous sodium sulphate was really in contact with the solutions even at temperatures below 33° C., and thus that an inversion of the decahydrate to the anhydrous salt takes place at various temperatures below 33°, depending upon the amount of sodium chloride contained in the solution in contact with the solid sodium sulphate.

In order to more satisfactorily demonstrate this the following experiment was performed: Two test-tubes, each containing a thermometer, were immersed in a large beaker of water. In the first test-tube was placed a saturated solution of sodium sulphate and also several large, well-formed crystals of the decahydrate. In the second test-tube was placed a solution saturated with respect to both sodium chloride and sodium sulphate, and also several large, well-formed crystals of the decahydrate. The temperature of the water in the beaker was slowly and gradually raised. At about 28° the crystals of the decahydrate in the second test-tube began to

cloud and become opaque around the edges, and as the temperature was maintained constant, this process continued until the whole mass was completely transformed from clear, translucent crystals of the decahydrate to an opaque mass of anhydrous salt. The crystals in the first test-tube remained unaltered. Thus it seems quite evident that the transformation of the decahydrate to anhydrous sodium sulphate at temperatures below 33°, is quite possible when the crystals are in contact with concentrated solutions of sodium chloride.

The change in the inversion temperature at which the decahydrate goes over to the anhydrous sodium sulphate, in the presence of a third substance in solution, which has just been described, is analogous to another case which has received attention in this laboratory. Van't Hoff and Armstrong,[1] Vater,[2] and Zunino[3] have recently called attention to the fact that gypsum, the dihydrate of calcium sulphate, was transformed to the hemihydrate at various, widely differing temperatures, depending upon the nature of the solution with which it was in contact. Cameron,[4] I believe, was the first to call attention specifically to this point. He investigated this case experimentally by a method similar to the one described in this paper, using a number of solutions of various salts, and various liquids. The facts brought out in this paper strengthen the view put forward regarding this phenomenon, and indicate the probability of its being found again in future studies of this nature.

In conclusion, I wish to acknowledge the assistance and advice of Dr. Frank K. Cameron, in carrying out this investigation and in the interpretation of the results.

BUREAU OF SOILS, U. S. DEPARTMENT
OF AGRICULTURE, WASHINGTON, D. C.

[1] Sitzungsber K. Preuss. Akad. Wiss., **28**, 559 (1900).
[2] *Loc. cit.*, **28**, 269 (1900).
[3] Gazz. chim. ital., **30**, 1, 333 (1900).
[4] Bulletin 18, page 37, Division of Soils, U. S. Department of Agriculture.

ON THE PREPARATION OF BROMOFORM BY ELECTROLYSIS.

By Paul Coughlin.

In 1884 E. Schering took out a patent (D. R. P. 29771) for the preparation of iodoform, bromoform, and chloroform by electrolysis. The patent specified that the respective halogen salts of the alkalies or alkali earths should be electrolyzed in the presence of alcohol, acetone, or aldehyde in a warm aqueous solution. Carbon dioxide was to be passed continuously into the electrolyte during the electrolysis.

Elbs and Herz,[1] in 1897, published the results of their investigation of the process covered by this patent in regard to the preparation of iodoform from alcohol and acetone. In regard to the preparation of bromoform they say: "Equally unsuccessful" (referring to their lack of success with acetone) "was an experiment on the electrolytic preparation of bromoform, in which the anode solution consisted of 6 grams soda and 10 grams potassium bromide in a mixture of 20 cc. alcohol and 100 cc. water; the anode density was 0.5 ampere per square decimeter; the temperature 60°. After 1.5 ampere hours the solution contained no bromoform."

I repeated the foregoing experiment with the same result that they obtained. Replacing the sodium carbonate by caustic soda did not change the result, nor was it changed when acetone was used instead of alcohol, and the two experiments repeated.

Having found previously that a temperature of 75° was necessary to obtain the best yield of iodoform from alcohol, I tried this temperature in preparing bromoform from alcohol and acetone. In order to maintain this temperature the electrolytic cell was placed in a water-bath, and to prevent loss of acetone or alcohol by evaporation the anode compartment —a porous cup—was fitted with a reflux condenser. The experiments with alcohol and carbonate, alcohol and caustic,

[1] Ztschr. Elektrochem., 4, 4, Aug. 20, 1897.

acetone and carbonate, and acetone and caustic, were repeated at 75° and then at 95°, but all resulted negatively.

The concentration of the solution was varied, and then the proportions of the various substances in the electrolyte, but without success. In many of these experiments an exceedingly penetrating, highly disagreeable odor showed the formation of brom acetones. To prevent this as much as possible, the acetone (or alcohol) was allowed to run into the electrolyte gradually during the electrolysis. Several of the former experiments were repeated with this modification, but in no case could any bromoform be detected.

The next attempt was with the electrolyte at room temperature. The electrolyte was 10 grams potassium bromide and 15 grams sodium carbonate in 75 cc. water and 20 cc. acetone, the anode and cathode being separated by a porous cup. A small drop of bromoform resulted from this electrolysis.

Having succeeded in obtaining a small yield of bromoform I endeavored, by systematic variation of the conditions that might affect the yield, to increase it to the maximum.

In all the following experiments the apparatus used consisted of a beaker of 250 cc. capacity in which was suspended a porous cup of 110 cc. capacity. The porous cup was made the cathode chamber, and in this was put a solution of 10 grams sodium carbonate in 100 cc. water; the cathode was an iron-wire gauze of about 60 sq. cm. superficial area on a side. The beaker contained the anode solution and the anode of platinum foil which had an area of 50 sq. cm. on each side. Usually two of these cells were connected in series, and in every case a copper voltameter was put into the circuit. Except when temperature conditions were tried, the cells were placed in vessels of cold water, so that the temperature varied but little from 25°. The time of the experiments was so varied that the amount of current used might be approximately the same for each experiment.

The formation of bromoform from acetone is expressed by the following equation:

$$6Br + (CH_3)_2CO + H_2O = CHBr_3 + CH_3COOH + 3HBr.$$

The presence of acetic acid in the electrolyte could readily be detected by the ethyl-ester test.

The bromoform was measured by being washed into a graduated tube and centrifugalized. The weight was found by considering the specific gravity to be 2.8. After some quantity had been collected, 10 cc. was distilled and practically all passed over between 140° and 155°.

In the first experiments the acetone was added to the electrolyte in equal quantities at intervals of ten minutes during the electrolysis, and the effect of varying the amount of sodium carbonate was tried; caustic soda was then substituted for the carbonate. The results are shown in the following table:

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Caustic. Grams.	Carbonate. Grams.	Anode density. Amp. per sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.
1	12	12	90		1	2.2	11.2	25°	2	2.2	0.7	19
2	12	12	90		5	2.2	9.5	25	2	2.2	0.4	11
3	12	12	90		2	2	4	25	2	2	1	30
4	12	12	90		3	2	4.5	25	2	2	1.1	33
5	12	12	90	1		2	11.2	25	2	2	0.3	9
6	12	12	90	2		2	5	25	2	2	drop	2
7	12	12	90	5		2	9.5	25	2	2	0.0	0
8	12	12	90	0.1		2	4	25	2	2	1.2	36

At the end of the electrolysis, in each case where the yield was very large, the electrolyte was colored by free bromine and had to be treated with caustic alkali or carbonate to free the bromoform of bromine. The limit of the yield with these conditions was soon reached; an experiment in which all the acetone was added at the beginning of the electrolysis showed the same yield that was obtained when the acetone was added gradually.

The fact that the yield decreased when enough carbonate was added at the beginning to keep the electrolyte clear, and that otherwise free bromine was present, suggested that it would be better to add the carbonate at intervals. When this was done a marked increase in the yield was shown. In the succeeding experiments the carbonate was added at such a rate that the electrolyte remained barely colored by free bromine. In some of the first experiments the carbonate was added in solution, but later, that the electrolyte might remain at constant volume, the solid was used with the same result.

The effect of temperature on the yield is shown by the following tables, the first having been made before the other conditions necessary to a maximum yield had been discovered :

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Carbonate. Grams.	Anode density. Amp. per. sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.
9	12	15	90	3	2.3	4.5	5°	2	2.3	2.0	53
10	12	15	90	3	2.3	4.3	15	2	2.3	2.1	55
11	12	15	90	3	2.3	4.3	25	2	2.3	2.24	59
12	12	15	90	4	2.3	4.2	35	2	2.3	1.54	40.8
13	25	10	75	6	3.8	5.5	10	1 : 15	2.37	3.08	82
14	25	10	75	6	3.8	5	15	1 : 15	2.37	3.64	97
15	25	10	75	6	3.8	4.3	20	1 : 15	2.36	3.7	99
16	25	10	75	6	3.84	4.2	25	1 : 16	2.4	3.8	100
17	25	10	75	6	3.8	3.8	30	1 : 15	2.36	3.73	100
18	25	10	75	6	3.6	3.8	35	1 : 20	2.37	3.4	90
19	25	10	75	6	3.85	3.8	40	1 : 15	2.4	3.08	81
20	25	10	75	6	4.0	3.5	50	1 : 10	2.4	3.08	81

Current density is a considerable factor in determining the yield, but in a modified way. This is seen by the following table. The first four experiments were made using a platinum gauze of 50 sq. cm. superficial area on a side, or a total of about 100 sq. cm. In the last four, the foil 5 x 10 cm. was used. These experiments would seem to indicate that the amount of current in proportion to the volume of the electrolyte has much to do with the result :

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Carbonate. Grams.	Anode density. Amp. per. sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.	
21	25	10	75	6	0.8	3.5	25°	2 : 18	1.9	2.52	84	
22	25	10	75	6	1.3	4.9		1 : 36	2.1	3.3	100	Gauze 100
23	25	10	75	6	1.8	4.5		1 : 15	2.3	3.64	100	sq. cm.
24	25	10	75	6	2	5		1	2.1	3.0	91	
25	25	10	75	6	1.6	3.5		2 : 18	1.9	2.38	79	
26	25	10	75	6	2.6	4.3		1 : 36	2.3	3.22	97	Foil 4 x 10
27	25	10	75	6	3	4.5		1 : 30	2.3	3.64	100	cm.
28	25	10	75	6	3.6	4.8		1 : 15	2.3	3.36	92	

A great many experiments had been tried, using only a little more than the theoretical amount of potassium bromide before the effect of increasing this amount was tried; but the maximum current efficiency was attained only when this amount was doubled, as shown below. The table shows that there is a definite maximum in this case, for when a greater amount of potassium bromide is added the yield decreases:

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Carbonate. Grams.	Anode density. Amp. per. sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.
29	10	10	75	6	3.6	4.2	25°	1 : 15	2.3	3.22	89
30	15	10	75	6	3.2	4.3		1 : 30	2.4	3.5	92
31	25	10	75	6	3.8	4.2		1 : 15	2.4	3.8	100
32	30	10	75	6	3.2	4.2		1 : 30	2.4	3.5	92
33	35	10	75	6	3.6	4		1 : 15	2.3	3.08	84

In the case of acetone, as of potassium bromide, the maximum current efficiency could not be attained when only the theoretical amount was used. The table shows, however, that the yield in regard to the amount of acetone was greatest when only the theoretical amount was used. The greater part of the excess of acetone remained unchanged in the electrolyte.

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Carbonate. Grams.	Anode density. Amp. per. sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.
1	25	1.5	75	6	3.6	3.8	25	1 : 20	2.37	0.84	22
2		2.5	75	6	3.6	4.3		1 : 15	2.3	1.12	31
3		5	75	6	3.6	4.6		1 : 15	2.3	2.24	62
4		7.5	75	6	3.7	4.3		1 : 15	2.36	3.08	82
5		10	75	6	3.8	4.2		1 : 16	2.4	3.8	100
6		15	75	6	3.8	4.8		1 : 16	2.4	3.88	100
7		20	75	6	3.7	5		1 : 15	2.36	3.73	100

In a few experiments in which alcohol was used instead of acetone, only a small amount of bromoform was formed. In

no case was the current yield greater than 10 per cent of theory.

ELECTROCHEMICAL LABORATORY,
INDIANA UNIVERSITY,
May 25, 1901.

NOTE ON THE RATE OF HYDRATION OF METAPHOSPHORIC ACID.

BY J. C. AND F. C. BLAKE.

It is well known that a water solution of metaphosphoric acid slowly changes to either pyro- or orthophosphoric acid at the ordinary temperature, according to the amount of water present. The rate of this change was investigated by Sabatier,[1] who employed the methods of acidimetry. We have reinvestigated the same reaction according to one of the methods recently outlined by Duane.[2] In his words: "In this

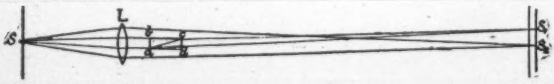


Fig. I.

method the basis of the measurement is the change in the index of refraction of the system, and it is applicable to those chemical systems only that are transparent. It is substantially the following: Rays of light from an illuminated slit S (Fig. I), passing through a long-focus lens L and the tube $a\ b\ c\ d$ form a distant image S_1 of S. The slit S is perpendicular to the plane of the diagram, which represents a horizontal section of the apparatus. The tube $a\ b\ c\ d$ has plane glass ends $a\ b$ and $c\ d$, and a plane glass plate $a\ c$ divides it into two wedge-shaped compartments. The ends $a\ b$ and $c\ d$ are not quite parallel to each other, so that if the two compartments are filled with liquids having the same index of refraction there will be a slight resultant refraction of the light rays that pass through the tube. The rays of light that pass outside of the tube will, therefore, form an image S_2 a little to

[1] Compt. rend., **106**, 63; **108**, 738, 804.
[2] Am. J. Sci., May, 1901.

one side of S_1. It is evident that if the liquid in one compartment (the wedge *a c d* for instance) is undergoing a chemical change its index of refraction in general will vary and the image S_1 will move sideways. The distance that S_1 has moved will be a measure of the change that has taken place in the index of refraction and, therefore, of the amount of substance in *a c d* that has reacted. The displacements of S_1 can be determined by comparing its distances from S_2 which remains stationary.

"In order to obtain a complete record of the position of S_1 a photographic plate, $S_1 S_2$, is placed in a vertical position at the images S_1 and S_2, and just in front of it is a screen. A narrow horizontal slit cut in the screen allows a small part of the light only to pass through. At any instant of time, therefore, there will be two small spots of light on the plate at the intersections of the two vertical images S_1 and S_2 with the projection of the slit on the plate. A system of cog-wheels allows the photographic plate to fall slowly during the reaction, so that two lines are drawn on it—one of them straight, due to the fixed image S_2, and the other curved, due to the moving image S_1. The curved line represents the reaction, in that the abscissas are proportional to the intervals of time and the ordinates represent (but are not proportional to) the quantities of the substance that have reacted. After the reaction is completed, the plate is drawn up and allowed to run down again, the image S_1 now tracing another line that is practically straight. This line may be taken as the zero line [the axis of x], and the distances between it and the curved one are (at least in some cases) proportional to the amounts of the original compounds left in the solution [at the corresponding times]."

Practically, the applicability of the method is quite limited, owing to the conditions of the experiment. The refractometer is a convenient instrument to use in determining whether the change in the index of refraction of any given system be sufficiently large to yield good results (methyl acetate and water were rejected on this account), as well as to ascertain approximately the necessary strength of the solution. Of

course, no ingredient can leave the field in the form of a gas or a precipitate. The use of a catalytic is permissible. The method would seem to be especially serviceable for those reactions whose constituents may hardly be gauged by chemical methods, such, for example, as those involving molecular rearrangement.

A suitable reaction having been decided upon, a measured amount of the solution is allowed to react completely and is then placed in one end of the tube. The same amount of a fresh solution is then mixed, and the clockwork started at the same instant. The position of the plate while at rest was recorded by a flash-light, whereby an image of the horizontal slit was photographed on the plate, which corresponds in position to the ordinate at the beginning of the reaction (the axis of y). The fresh solution is then placed in the other end of the tube, and, after adjusting the focus, the plate is exposed. It might be of practical importance to add that considerable difficulty was experienced in adjusting the focus, due to the fact that the fresh solution just introduced into the tube is not entirely homogeneous, especially where it comes in contact with the glass to which traces of the former solution always adhere. If the focus is not readily adjustable, so much of the best part of the curve is lost that the plate is practically worthless. Therefore, after many failures, the following method was adopted: Place in each end of the tube a solution that has already reacted and adjust the lens so that the beam through the solution will be in focus on the plate. If this causes the side-light to blur too much to give a distinct image at S_2, a separate lens or a separate source of light will have to be introduced for this purpose. A fresh solution is then introduced into one end of the tube and the plate exposed. It will usually appear to the eye that the beam through the solution is no longer in focus; but experience teaches that it will, nevertheless, make an impression on an "extra-sensitive" plate as a fine line, becoming even finer as the fresh solution becomes more homogeneous. The plate herewith represented is not one of the best so far as the focus is concerned, but the improvement in this respect may readily be observed.

We call attention to the following precaution: After having been once set up the apparatus must remain absolutely fixed, not only during the few days necessary to complete one reaction, but during the time necessary to complete the whole series of reactions, especially those of the whole solution and the corresponding partial solutions. The ordinary precautions are not sufficient to guard against this source of error, since the plan of the apparatus is such that the slightest motion of the slit, the lens, or the tube, is magnified many times on the plate. Many plates were spoiled owing to this source of error without apparent explanation. In order that two plates may be comparable, the line traced by the side-light on the one must overlie the corresponding line on the other when the plates are superimposed, in order to show that the vertical slit and the lens have not been moved; the line traced by the beam through the solution after the reaction is completed (the axis of x) on the one must overlie that of the other, in order to prove that the tube containing the solution has not been moved sidewise or turned about a vertical axis, and in order to prove that the two fresh solutions were of the same strength (this applies especially to partial solutions); and, of course, the side-light on any one plate must be represented by only a single line, no matter how many times the plate has been exposed, in order to prove further that the plate has not been moved.

In working with metaphosphoric acid, owing to the remarkable deliquescence of the substance, each specimen of the acid had to be prepared afresh and the weighing could be accomplished with only approximate exactness. One specimen, prepared by dissolving the anhydride in water and heating in a platinum crucible until the liquid remained quiet over an ordinary Bunsen burner except for the escape of white fumes, contained 99.1 per cent of metaphosphoric acid; although other specimens may have contained an amount of phosphorus corresponding to more than 100 per cent of metaphosphoric acid, as is usually the case, owing to the presence of anhydride. The customary difficulty was experienced in obtaining an acid sufficiently free from alkalies to be freely soluble in water.

The plate figured herewith represents the curve obtained as above described when 4 grams of metaphosphoric acid were dissolved in 5 cc. of water at 18°.5, the temperature being kept nearly constant until the reaction was over. About nine minutes were required for solution. The second line from the top is the record left by the side-light, showing that the apparatus was not moved. The other four horizontal lines are the record of the reaction during four successive nights, the lowest one representing the end reaction (the axis of x), it having been previously determined that the reaction is completed in four days. This was done by allowing the plate to run down a fifth night, the line thus traced being identical with the line traced the fourth night. That the reaction was completed in the time specified is further shown, though not with the same degree of precision, by the fact that the line for the fourth night and the line traced by the side-light are measurably parallel. The vertical line at the right was due to the flash-light and represents the position of the plate at the beginning of the reaction (the axis of y). The distance between this line and the beginning of the principal curve represents the time (nearly half an hour) necessary for introducing the solution into the tube and adjusting the focus. By having the focus pre-adjusted as indicated above, this interval was much reduced. The ordinates were drawn with the the dividing engine, and represent intervals of thirty minutes each.

Two lenses, L_1 and L_2, were used instead of one, L, being between the tube and the plate, and very near the tube in order not to neutralize the dispersion. The distance $S L_1 =$ 15.4 cm.; $L_1 L_2 =$ 19.4 cm.; $L_2 S_2 =$ 214 cm.; $a\,b =$ 0.4 cm.; $a\,d =$ 5.6 cm.; $L_1 a =$ 5.8 cm.; $d L_2 =$ 8 cm. The width of the vertical slit S was 0.05 mm.; the width of the horizontal slit in front of the plate was 0.2 mm., and its distance from the plate was 0.6 cm. In order to improve the focus still further, the ends of the tube were covered with a black cloth having a vertical slit 0.27 cm. in width. The width of this slit might advantageously be still further reduced. The source of light was an ordinary incandescent electric bulb.

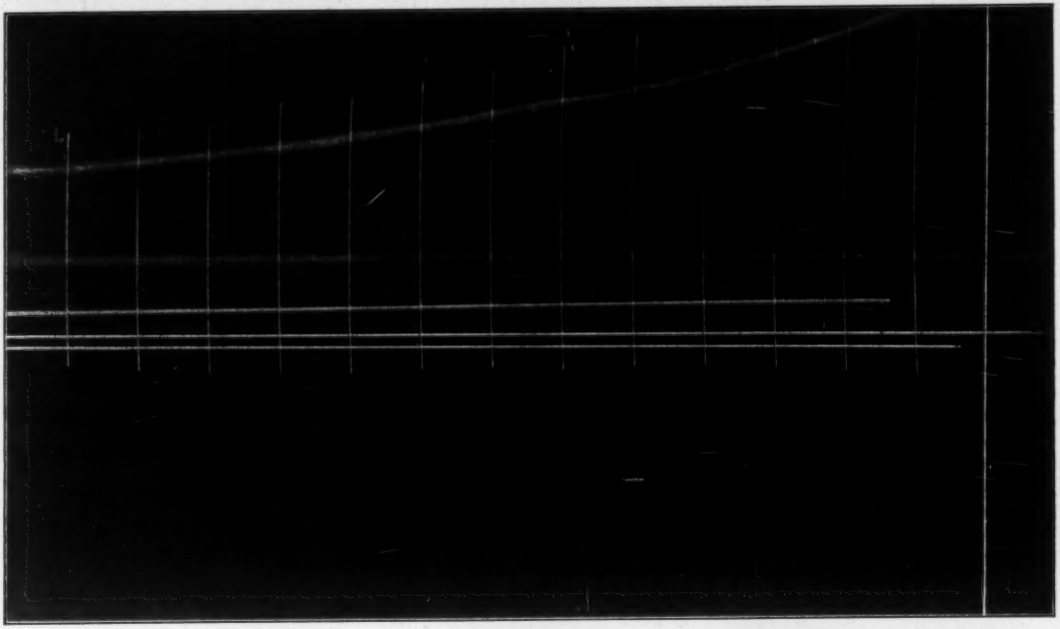


PLATE I.

In the paper last referred to, it is presumed that in most cases the amounts of the original substances remaining unchanged at any given time will be directly proportional to the corresponding ordinate of the curve thus obtained; that is, that this curve should fulfil the conditions of Guldberg and and Waage's law, that the rate at which the reaction proceeds is proportional to the amount of unchanged substance left in the solution. The foregoing assumption was to be proved, however, by placing in one end of the tube a mixture containing known amounts of new and old solution, and ascertaining whether the largest ordinate so obtained bore the same ratio to the largest ordinate obtained for a wholly fresh solution that the amount of fresh acid in the mixture bore to the amount of acid in the wholly fresh solution. For a solution of metaphosphoric acid so mixed, containing equal amounts of new and old solution, the largest ordinate was found to be only 40 per cent of the largest ordinate of the corresponding whole solution, or four-fifths of what it should have been to uphold the assumption. Several series of such plates have been obtained, checking as closely as might be expected (within 1 per cent) at 40 per cent. Therefore, as the curve photographed does not bear the simple relation above mentioned, it will be necessary to determine the ratio of the ordinates of the curve photographed to the amounts of fresh acid in the solution for several points by mixing new and old solutions in various known proportions, and from the points thus located to plot the curve that really corresponds to the amounts of metaphosphoric acid remaining unchanged at each instant of time. Since this has not been done and the apparatus has been taken down, it will be necessary to begin a new series of curves. Of course, no attempt can be made to determine the equation of the curve until this correction has been made. Owing to the force of circumstances, this cannot be undertaken for some time and we merely report progress. The previous work of Sabatier increases rather than diminishes the interest with which we await the opportunity to compare results obtained by methods so widely different.

We gratefully acknowledge our indebtedness to Dr. Wm. Duane for assistance and advice throughout the course of the work.

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NOTES.

Radio-Lead.

In a note which appeared in the last volume of this JOURNAL,[1] attention was called to the important results obtained in the course of recent investigations on radio-active substances. Brief mention was made of the active lead salts obtained by Hofmann and Strauss[2] from a number of uranium minerals such as bröggerite, cleveite, pitchblende, alvite, samarskite, euxenite, and uranium mica. Since that time these authors have published the results of further investigations along the same line.[3] It now appears that these salts contain a new element closely related to lead.

By appropriate methods they are able to separate from the minerals, or from uranium residues, chloride of lead mixed with "radio-lead" chloride, and the chloride of still another new element which appears to be very closely related to ruthenium, as we should expect from its approximate atomic weight, 100.92. It is probably the homologue of manganese. It was not fully investigated.

From the more soluble portions of the mixed chlorides they obtained, besides the above-mentioned element, the strongly active radio-lead. Its sulphate was analyzed and found to contain about 41.7 per cent SO_4. If the metal be bivalent in the sulphate, this would indicate an atomic weight of 171.96, so that it might be regarded as the homologue of tin. Radio-lead can be precipitated from slightly acid solutions by hydrogen sulphide, its sulphate is insoluble in dilute sulphuric acid, its salts dissolve in caustic potash and can be precipitated by hydrogen sulphide. The nitrate is soluble in water, and from this solution it is almost completely precipitated by ammonium carbonate. Unlike lead, its chromate is not decomposed by sulphuric acid. Its chloride is more soluble than lead chloride, and its sulphide is at once decomposed by fuming hydrochloric acid. Lead sulphate gives a blue light when under the influence of the cathode rays; radio-lead sulphate gives a bright-blue light and is afterwards phospho-

[1] This JOURNAL, 25, 77 (1901).

[2] Ber. d. chem. Ges., 33, 3126 (1901).

[3] *Ibid.*, 34, 8, 907, 3033 (1901). See also Hofmann, Korn, u. Strauss: *Ibid.*, 34, 407.

re scent. The active sulphate has an intense rose color when heated in the air to 500°. The chloride often has a similar color.

Radio-lead sulphate acts on the photographic plate through glass, aluminium, caoutchouc, paper, and air, and much more strongly than polonium obtained at the same time from the same minerals. It discharges the electroscope, but not as rapidly as polonium salts. Even when exposed to direct daylight for two months there was no change in its photographic activity. From this and from its action through aluminium it differs from the phosphorescent sulphides of the alkaline earths. The sulphate emits Becquerel rays. It was shown that radium and polonium purposely mixed with lead salts could easily be separated by the method used in preparing radio-lead sulphate, and the resulting lead sulphate was inactive. Further, radio-lead is unlike radium, polonium, and actinium in that its sulphate alone acts photographically. The sulphide, chloride, iodide, chromate, carbonate, and oxide made from strongly active sulphate are inactive, but regain their power when changed back into the sulphate. Since the activity ceases after some months it is evident that radium is absent. The renewal of activity under the influence of the cathode rays shows that polonium is not present. When the sulphate is partly changed into sulphide by heating with sulphur, it becomes inactive. The activity is greatly increased by heating to 450° for fifteen hours, and also by evaporating with sulphuric and nitric acids.

It was found that the sulphate, sulphide, chloride, iodide, chromate, and carbonate are alike in their action on the electroscope.

When equal amounts of radio-lead sulphate and of lead sulphate containing radium were placed on the glass side of a photographic plate it was seen that the radium had acted on the farther side of the gelatin layer, but the radio-lead acted only on the side next to the glass.

Since only the sulphate acts photographically while all the salts discharge the electroscope, it is evident the photographic radiation is not the same as that which produces the latter effect. Having in mind the latest work on thorium radiation and the discharge of electroscopes in the higher strata of the air, one might imagine that a tenuous, almost imponderable, substance adheres to radio-active substances, and by its gradual escape discharges the electroscope, and, secondarily, produces photographic effects. But this is not in agreement with the fact that heating to 450° increases the radio-activity.

It is probable that there is within the atoms some activity that causes the emission of rays of different wave-lengths, and, consequently, of different properties. It was at first thought that the activity might be due to positive charges due to the cathode rays. If this were the case, the anode rays should destroy this effect, but it was found that they produced a slightly greater activity. Neither can they be cathode rays, for they penetrate glass or a layer of air 1 cm. in thickness without appreciable weakening of effect.

This work of Hofmann and Strauss has been severely criticized by Giesel,[1] who first pointed out that it would be very difficult to obtain new radio-active substances in pure condition from such small quantities of the earths as 100 grams. He was of the opinion that the effects noticed must be due to the presence of very small quantities of the intensely active substances already known, or else to induced activity. More recently[2] he takes up the discussion anew, and repeats the experiments with two samples of radio-lead sulphate prepared by Hofmann and Strauss. His results are, in some respects, in direct contradiction to theirs. He finds that "the sulphate does not lose its Becquerel-radiation in three-fourths of a year, and it is not caused to give new or increased Becquerel-radiation by the cathode rays. All the compounds, and not the sulphate alone, act on the photographic plate. The apparently contradictory result of Hofmann and Strauss is explained by their arrangement of the experiment which does not exclude a secondary action of phosphorescent light. Radio-lead sulphate emits a mixture of Becquerel rays and light rays which are produced constantly by the former." When the plate is wrapped in black paper the action of the light rays is prevented and on long exposure the Becquerel rays finally act. Radio-lead sulphate and the carbonate, chloride, and sulphide prepared from it produced exactly the same effect under these conditions. He was able to detect a very faint phosphorescence in the sulphate.

Hofmann and Strauss found that the radio-lead rays acted on the bromide of silver layer on the side next to the glass, but the radium rays acted on the farther side. This is due to the fact that the light rays from the radio-lead sulphate are not able to penetrate the sensitive film as readily as the Becquerel rays.

Repeating the experiment of mixing radium and lead salts and then separating the two, he obtained an active lead sulphate

[1] Ber. d. chem. Ges., **33**, 19, 3569 (1900).
[2] Ber. d. chem. Ges., **34**, 3772 (1901).

in which radium could not be detected chemically. This was done by allowing the mixed solutions to stand for eight days before the separation. This was analogous to his previous experiments with bismuth.[1] The sulphide of lead so obtained, and the iodide made from it, were both active. He is of the opinion that Hofmann and Strauss have not yet proved the existence of a new radio-active element in radio-lead.

The new unnamed substance,[2] which acts chemically like lead and was discovered in uranium mother-liquors, shows no diminution of its intense activity after standing a year. In this respect it resembles radium and actinium. Polonium material shows a slight activity after two years. Fresh preparations lose their activity rapidly, but the rate of loss continually decreases, especially if the polonium be mixed with a large proportion of lead chloride.

He was able to show that the water of crystallization distilled from radium barium bromide is strongly active. That this is not due to radium carried over with the steam is shown by its loss of activity after a few days. Nearly all colorless or slightly colored solids became luminous under the influence of the radium rays, and the same is true of liquids such as water, and especially petroleum. The luminous zone does not extend far into the liquid. C. E. W.

On the Existence of Ammonium.

The evidence in favor of the metallic nature of ammonium was summed up in a note in the last volume of this JOURNAL.[3] Le Blanc's work on ammonium amalgam formed by the electrolysis of ammonium salts at a low temperature seemed to have "removed the last experimental evidence against the metallic nature of ammonium." Quite recently Otto Ruff[4] attempted to obtain ammonium by the electrolysis of ammonium iodide dissolved in liquid ammonia. A tube, somewhat like an inverted Y with electrodes fused into the lower ends, was partly filled with potassium iodide. It was then cooled with liquid air and alcohol and dry ammonia was condensed in it. On passing an electric current through it iodine was set free at the positive pole, and at the negative pole were seen drops of a light, mobile, copper-colored liquid with a metallic appearance. These rose to the top and dissolved, forming a solution of an intense blue color. The substance was shown to be potassium ammonium, $K.NH_3$.

[1] Verh. d. phys. Ges., 5 Januar, 1900.
[2] Ber. d. chem. Ges., 33, 19, 3570 (1900).
[3] This JOURNAL, 25, 431 (1901).
[4] Ber. d. chem. Ges., 34, 2604 (1901).

The electrolysis of ammonium iodide was next undertaken, but even when the solution was cooled down to its freezing-point, —95°, nothing but hydrogen was formed at the negative pole, and not a trace of blue color was seen in the solution. It was thought that some ammonium might be formed at high pressures, and the experiment was repeated with the upper end of the tube sealed, and the whole cooled to —95°. After the current had passed for five hours, and an estimated pressure of 60 atmospheres had been obtained, there was still no evidence of the formation of ammonium. There was also no ammonium amalgam formed when mercury was used as the cathode.

The author thinks that ammonium may possibly be obtained by working at still lower temperatures and with greater pressures. A suitable solvent for these conditions is unknown. Ammonium is not to be regarded as a true analogue of the alkali metals, but resembles the easily dissociated alkali-ammonium compounds such as $K.NH_3$, $Na.NH_3$, and $Li.NH_3$. It should be written $H.NH_3$ instead of NH_4.

C. E. W.

REVIEWS.

DIE HETEROGENEN GLEICHGEWICHTE VOM STANDPUNKTE DER PHASENLEHRE, von DR. H. W. BAKHUIS ROOZEBOOM, Professor an der Universität Amsterdam. Erstes Heft, DIE PHASENLEHRE-SYSTEME AUS EINER KOMPONENTE. Mit 54 eingedruckten Abbildungen. Druck und Verlag von Friedrich Vieweg und Sohn, Braunschweig. 1901. pp. 221.

There are few subjects in physical chemistry which are discussed more freely to-day than the phase rule, and few the meaning of which is less clearly understood. There are those persons who tell us that the phase rule is the one generalization of importance in physical chemistry, and that everything in physical chemistry, not to say in chemistry, should center around it.

On the other hand, there are those who will have very little to do with the phase rule even as applied to physical chemistry, and among this number can be mentioned some who stand in the very front rank of physical chemists.

The intermediate stage is, however, represented here as in so many other fields. Those who belong to this class regard the phase rule as an important generalization, which correlates a large number of more or less isolated facts already established, and which also suggests new lines of investigation. They regard the phase rule as one of the three or four impor-

tant generalizations that have been reached by modern physical chemistry, and upon which it is based. The author of the book in question belongs to this class.

It should be pointed out that much of the most important experimental work bearing upon the phase rule has been done by Roozeboom and his pupils. The book is, therefore, written by one whose knowledge of the phase rule has been applied in the laboratory.

The part of the book which is at hand deals only with systems containing one component. A brief historical introduction, including homogeneous and heterogeneous equilibrium, the phase rule, non-variant, mono-, di-, and polyvariant systems, is followed by a discussion of the various systems with one component. These include equilibrium between a liquid and a gaseous phase, equilibrium between a solid and a gaseous phase, equilibrium between a solid and a liquid phase, and equilibrium between two solid phases. The "triple-points" in the cases of solid, liquid and gas ; solid, solid, and gas ; solid, solid, and liquid ; and solid, solid, and solid, are considered at some length, and in such a clear and concise manner that the reader can scarcely fail to grasp their significance.

As far as one can judge of a book from the appearance of the first third of it, the work in hand is by far the clearest and most intelligible that has thus far been written on the phase rule. It is safe to predict that the completed work will contribute much to a better understanding of this important generalization, which has been frequently disregarded because of the unnecessary complexity in which it has been shrouded.

The second portion of the book will deal with systems of two components, and the third with three and more components. H. C. J.

JAHRBUCH DER ELEKTROCHEMIE, BERICHTE ÜBER DIE FORTSCHRITTE DES JAHRES 1900. Unter Mitwirkung der HERRN PROF. DR. K. ELBS, Giessen, PROF. F. W. KÜSTER, Clausthal, und Privat-docent DR. H. DANNEEL, Aachen. Herausgegeben von DR. W. NERNST, o. Professor an der Universität Göttingen, Direktor des Instituts für physikalische Chemie und Elektrochemie ; und DR. W. BORCHERS, o. Professor an der Technischen Hochschule Aachen, Vorstand des Laboratoriums für Metallhüttenkunde und Elektrometallurgie. vii Jahrgang. Verlag von Wilhelm Knapp, Halle, A. S. 1901. pp. 596.

The "Jahrbuch der Elektrochemie" contains, as is well known, a brief survey of the work of the year in electrochemistry. This subject has two distinct phases, the scientific and the practical, and each has acquired the greatest prominence in the last few years. Each side of the subject is represented

by one of the ablest men of the day, and this insures a masterly treatment of the whole subject. The collaborators of Nernst and Borchers are men of high standing both in the science and application of chemistry.

For the convenience of those who use the book the material has been beautifully systematized. The scientific portion treats first of such general matters as lecture experiments, books which have appeared, description of methods, apparatus which has been devised, etc. The broad subject of conductivity is taken up and its applications to special problems, such as the dissociating power of solvents, the constitution of inorganic and organic compounds, the electrical conductivity of solids, and the like. One of the most interesting sections in this part of the work is that which has to do with electrolysis and polarization. The theory of electrolysis advanced by Le Blanc and now generally accepted, as well as his own beautiful investigations on polarization, have brought the whole subject very much to the front in the last few years. Since the work of Nernst on the electromotive force of primary cells, few investigations in the field of electrochemistry can be compared in importance with it, and this is shown by the amount of work done yearly in this field.

The material in applied electrochemistry is also well systematized under the general heads of production of electrical energy, electrolysis, including the production of the non-metals, the metals, inorganic compounds, and organic compounds. This is followed by a discussion of forms of apparatus devised for use in applied electrochemistry.

The book is useful to all who are interested in any phase of electrochemistry, but especially to those who do not have access to the current literature of the subject. H. C. J.

THE ELEMENTS OF QUALITATIVE ANALYSIS. By WM. A. NOYES, PH.D., Professor of Chemistry in the Rose Polytechnic Institute. Fifth edition, revised. New York: Henry Holt & Co. 1901.

Prof. Noyes' book is well known as one of the best brief laboratory manuals in use. In the present edition he has revised the scheme for the systematic detection of acids, employing in the main the methods suggested by Abegg and Herz.

A few pages of the introduction are given to a brief sketch of the theory of solutions. E. R.